U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-257 284

Federal Guidelines Pretreatment of Pollutants Introduced into Publicly Owned Treatment Works

Environmental Protection Agency

Oct 73

FEDERAL GUIDELINES

PB 257 284

PRETREATMENT OF POLLUTANTS INTRODUCED INTO PUBLICLY OWNED TREATMENT WORKS

OCTOBER 1973

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF WATER PROGRAM OPERATIONS
WASHINGTON, D.C. 20460

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

160

FOREWORD

In response to the Federal Water Pollution Control Act Amendments of 1972 (P.L. 92-500), this country has undertaken an unprecedented program of cleaning up our Nation's waters. There will be a substantial investment by Federal, State, and local government as well as by private industry in treatment works to achieve the goals of the Act. It is important that the investment in publicly owned treatment works be protected from damage and interference with proper operation.

These guidelines were developed by the Environmental Protection Agency in accordance with Section 304(f) of the Act. It is important to note the clear requirements in the Act that there be both national pretreatment standards, Federally enforceable, and pretreatment guidelines to assist States and municipalities in developing local pretreatment requirements. Some factors in pretreatment are not amenable to a national standard. The Environmental Protection Agency therefore encourages the establishment of local pretreatment requirements, tailored to the conditions at a specific publicly owned treatment works. Such requirements are considered essential to ensure compliance with permits issued under the National Pollutant Discharge Elimination System.

The guidelines were the subject of numerous extensive reviews, both within the Government and by affected segments of the public. All of the many comments were carefully considered in arriving at this publication. It is the intention of the Environmental Protection Agency to revise these guidelines from time to time as additional technical information becomes available and as industrial effluent guidelines are issued pursuant to Section 304(b) of the Act. The most valuable source of information for revisions, however, will be actual experiences of those using the guidelines. All users are encouraged to submit such information to the Director of the Municipal Waste Water Systems Division, Office of Air and Water Programs, Environmental Protection Agency, Washington, D.C. 20460.

John Quarles

Acting Administrator

TABLE OF CONTENTS

		Page No.
SECTION I	INTRODUCTION	1
	1. Purpose	1
	2. Authority	1
	3. Definitions	2
	4. The Federal Water Pollution Control Amendments of 1972	3
SECTION II	EFFLUENT LIMITATIONS AND NPDES PERMITS	4
	5. NPDES Municipal Permits	4
	6. Effluent Limitations for Publicly Owned Treatment Works	5
SECTION III	JOINT TREATMENT AND PRETREATMENT	6
	7. Joint Treatment	6
	8. Pretreatment Policy	7
	9. Federal Pretreatment Standards	7
SECTION IV	STATE AND LOCAL PRETREATMENT REQUIREMENTS	10
	10. Objectives	10
	11. Pretreatment Information	10
	12. Pretreatment Ordinance	13
	13. Example Calculations	14
	14. Other Considerations	15
APPENDIX A	Pretreatment Standards (40 CFR 128)	A-1
APPENDIX B	Secondary Treatment Information (40 CFR 133)	B-1
APPENDIX C	Information on Materials Which Inhibit Biological Treatment Systems	C-1

TABLE OF CONTENTS
(continued)

Page No.

APPENDIX D Information on Pretreatment Unit Operations D-1-1

- Annex 1-Paper and Allied Products D-1-1
- Annex 2-Dairy Products D-2-1
- Annex 3-Textiles D-3-1
- Annex 4-Seafoods D-4-1
- Annex 5-Pharmaceuticals D-5-1
- Annex 6-Leather Tanning and Finishing D-6-1
- Annex 7-Sugar D-7-1
- Annex 8-Petroleum Refining D-8-1
- Annex 9-Meat Products D-9-1
- Annex 10-Grain Milling D-10-1
- Annex 11-Fruit and Vegetable D-11-1
- Annex 12-Beverages D-12-1
- Annex 13-Plastic and Synthetic Materials D-13-1
- Annex 14-Blast Furnaces, Steel Works, and Rolling and Finishing D-14-1
- Annex 15-Organic Chemicals D-15-1
- Annex 16-Metal Finishing D-16-1
- Annex 17-Other Industries D-17-1
  - Inorganic Fertilizer D-17-2
  - Electric and Steam Generation D-17-4
  - Aluminum D-17-6
  - Flat Glass, Cement, Lime, Concrete Products, Gypsum, and Asbestos D-17-8
  - Inorganic Chemicals D-17-10
  - Industrial Gas Products D-17-12

Federal Guidelines

Pretreatment of Pollutants Introduced Into Publicly Owned Treatment Works

SECTION I

INTRODUCTION

1. Purpose

These guidelines are established to assist municipalities, States, and Federal agencies in developing requirements for the pretreatment of wastewaters which are discharged to publicly owned treatment works. The Guidelines also explain the relationship between pretreatment and the effluent limitations for a publicly owned treatment works.

The U.S. Environmental Protection Agency (EPA) has published Pretreatment Standards in 40 CFR 128 (Appendix A). The standards will be enforceable by the EPA. These guidelines provide technical information useful to States and municipalities in establishing pretreatment requirements to supplement the Federal pretreatment standards.

2. Authority

Authority for these guidelines is contained in Section 304(f) (1) of the Federal Water Pollution Control Act Amendments of 1972 (the Act), which states:

> "For the purpose of assisting States in carrying out programs under Section 402 of this Act, the Administrator shall publish . . . guidelines for pretreatment of pollutants which he determines are not susceptible to treatment by publicly owned treatment works. Guidelines under this subsection shall be established to control and prevent the discharge . . . of any pollutant which interferes with, passes through, or otherwise is incompatible with such works".

3. Definitions

Compatible Pollutant:

Biochemical oxygen demand, suspended solids, pH, and fecal coliform bacteria, plus additional pollutants identified in the NPDES permit if the publicly owned treatment works was designed to treat such pollutants, and in fact does remove such pollutants to a substantial degree. The term substantial degree is not subject to precise definition, but generally contemplates removals in the order of 80 percent or greater. Minor incidental removals in the order of 10 to 30 percent are not considered substantial. Examples of the additional pollutants which may be considered compatible include:

Chemical oxygen demand
Total organic carbon
Phosphorus and phosphorus compounds
Nitrogen and nitrogen compounds
Fats, oils, and greases of animal or vegetable origin (except as prohibited where these materials would interfere with the operation of the publicly owned treatment works).

Incompatible pollutant:

Any pollutant which is not defined as a compatible pollutant.

Joint Treatment Works:

Treatment works for both non-industrial and industrial wastewater.

Major Contributing Industry:

A major contributing industry is one that: 1) has a flow of 50,000 gallons or more per average work day; 2) has a flow greater than five percent of the flow carried by the municipal system receiving the waste; 3) has in its waste a toxic pollutant in toxic amounts as defined in standards issued under Section 307 (a) of the Act; or 4) has a significant impact, either singly or in combination with other contributing industries, on a publicly owned treatment works or on the quality of effluent from that treatment works.

Pretreatment:

Treatment of wastewaters from sources before introduction into the joint treatment works.

4. The Federal Water Pollution Control Act Amendments of 1972

The Act established a national system for preventing, reducing, and eventually eliminating water pollution. The ultimate goal is to eliminate the discharge of pollutants into the navigable waters of the United States.

Under the National Pollutant Discharge Elimination System (NPDES), all point sources (including publicly owned treatment works) must obtain a permit for the discharge of wastewaters to the navigable waters of the United States.

The Act further requires that, as a minimum intermediate objective, all point sources other than publicly owned treatment works treat their wastewaters by the application of the best practicable control technology. Subsequently, the minimum requirement for industrial wastewaters would be the application of best available treatment technology. For publicly owned treatment works, the initial objective is secondary treatment, followed by best practicable treatment technology.

Monitoring for compliance with effluent limitations and pretreatment requirements will be in accordance with EPA guidelines established under Section 304 and implemented under Section 308 of the Act.

5. NPDES Municipal Permits

Procedures developed under Section 402 of the Act will provide the details for implementation of permit programs. The purpose of the following discussion is to highlight the relation between the permit programs and the pretreatment standards and guidelines.

Under the National Pollutant Discharge Elimination System (NPDES), all point sources (including publicly owned treatment works) must obtain a permit for the discharge of wastewaters to the navigable waters of the United States. Permits will not be required for industrial sources discharging into publicly owned treatment works.

The pretreatment standards (Appendix A) will be directly enforceable by EPA on industry.

The effluent limitations for a pollutant in the discharge from a publicly owned treatment works will be individually determined by the permitting agency, based on information supplied by the municipality. These effluent limitations will be included in the discharge permit issued to the municipality for the publicly owned treatment works.

Additionally the permit for a publicly owned treatment works will require provisions for adequate notice to the permitting agency of:

a. New introductions into such works of pollutants from any source which would be a new source as defined in Section 306 of the Act if such source were discharging pollutants.

b. New introductions of pollutants into such works from a source which would be subject to Section 301 of the Act if it were discharging such pollutants.

c. A substantial change in volume or character of pollutants being introduced into such works by a source already discharging pollutants into such works at the time the permit is issued.

This notice will include information on the quantity and quality of the wastewater introduced by the new source into the publicly owned treatment works, and on any anticipated impact on the effluent discharged from such works.

The permit programs developed under Section 402 of the Act should be consulted for details regarding permit application.

6. Effluent Limitations for Publicly Owned Treatment Works

There are various sources of effluent limitations, including:

a. Effluent limitations for publicly owned treatment works (Section 301(b) of the Act). Secondary treatment information is contained in 40 CFR Part 133 (Appendix B).

b. Toxic Effluent Standards or Prohibitions (Section 307 (a) of the Act).

c. Water Quality Standards (Section 303 of the Act).

The most stringent limitation for each pollutant will govern.

SECTION III

JOINT TREATMENT AND PRETREATMENT

7. Joint Treatment

Joint treatment of industrial and municipal wastewaters in the same treatment works is generally a desirable practice. Treatment of the combined wastewaters can benefit the environment, the municipality, and industry if properly designed and operated.

Some of the advantages of joint treatment are:

a. Increased flow which can result in reduced ratios of peak to average flows.

b. Savings in capital and operating expenses due to the economics of large-scale treatment facilities.

c. Better use of manpower and land.

d. Improved operation (larger plants are potentially better operated than smaller plants).

e. Increased number of treatment modules with resultant gains in reliability and flexibility.

f. More efficient disposal of sludges resulting from treatment of wastewaters containing compatible pollutants.

In some cases, the characteristics of the industrial wastewaters may be beneficial in the publicly owned treatment works processes. For example, some industrial wastewaters contain organic material but are devoid of the nutrients required for biological treatment. In joint biological treatment the nutrients are present in the domestic wastewater and consequently do not have to be added (as they would in separate industrial treatment). For a plant required to remove nutrients, the joint biological treatment of nutrient-free organic industrial wastes would result in lower amounts of nutrients to be removed in a subsequent process.

There may be characteristics present, however, which make a wastewater not susceptible to joint treatment if introduced directly into the municipal system. In such cases, it will be necessary to pretreat the wastewater.

8. Pretreatment Policy

The following are basic pretreatment policy considerations used in developing these guidelines:

a. Joint treatment of domestic wastewaters and adequately pretreated industrial wastewaters is encouraged where it is the economical choice.

b. In-plant measures to reduce the quantity and strength of industrial wastewater flows can be beneficial to joint treatment, and should be encouraged.

c. Pretreatment for removal of compatible pollutants is not required by the Federal pretreatment standards.

d. In recognition of the broad spectrum of industries, waste constituents, and treatment plants, State and municipal pretreatment requirements should be based on an individual analysis of the permitted effluent limitations placed on a publicly owned treatment works and on the potential for adverse effects on such works.

9. Federal Pretreatment Standards

EPA has issued standards in 40 CFR Part 128 for pretreatment of pollutants introduced into publicly owned treatment works (Appendix A). These standards are designed to protect the operation of a publicly owned treatment works and to prevent the introduction of pollutants into publicly owned treatment works which would pass through such works inadequately treated.

The pretreatment standards are intended to be national in scope, i.e. generally applicable to all situations. In many cases, it will be necessary for a State or a municipality to supplement the Federal Standards with additional pretreatment requirements which take into account local conditions. The purpose of these guidelines is to provide information to States and municipalities to assist in the development of these supplemental pretreatment requirements. The following paragraphs describe the basis and extent of the Federal pretreatment standards.

Section 128.131 of the Standards (Appendix A) is designed to protect the operation of publicly owned treatment works. Wastes which are prohibited from introduction into publicly owned treatment works are listed. This Section is applicable to non-domestic users only.

Section 128.133 is designed to prevent the introduction of incompatible pollutants to publicly owned treatment works which would pass through such works inadequately treated. Any pollutant that is not a compatible pollutant as defined in Section 128.121 is by definition incompatible. Section 128.133 is applicable only to "major contributing industries" as defined. Pretreatment is required for incompatible pollutants to the levels of best practicable control technology currently available as defined for industry categories in guidelines issued pursuant to Section 304(b) of the Act. Provision is made for the Administrator to segment the industrial users of municipal systems as a special category for the purposes of defining best practicable control technology currently available. Provision is also made to permit a less stringent pretreatment standard for an incompatible pollutant if the municipality is committed in its NPDES permit to remove a specified percentage of the incompatible pollutant. These requirements are based on the premise that incompatible pollutants introduced into a publicly owned treatment works generally should not pass through such works in amounts greater than would be permitted for direct discharge.

Biochemical oxygen demand, suspended solids, pH, and fecal coliform bacteria, which are defined as compatible, are the pollutants used to describe the effluent quality attainable by secondary treatment in 40 CFR Part 133 (Appendix B). Not later than July 1, 1977, secondary treatment effluent limitations must be met by all publicly owned treatment works which discharge into navigable waters unless more stringent effluent limitations are necessary to ensure compliance with water quality standards or toxic effluent standards.

The terms compatible and incompatible pollutant should not be misinterpreted. For incompatible pollutants, it will be necessary for the municipality to assess the capabilities of its treatment works in order to determine whether it can make a commitment in its NPDES permit to remove some percentage of the incompatible pollutants in the treatment works. Such a commitment might be made if there is some removal of incompatible pollutants in the treatment works which occurs as an incident to the removal of compatible pollutants. In this case it must be determined that the incidental removal can be relied upon and will not cause harm to the treatment works or interfere with its operation (including sludge handling and disposal processes).

There will also be situations when the Federal pretreatment standards (without credit for removal in the publicly owned treatment works) will not be sufficient to protect the opeation of the publicly owned treatment works. This might be the case when the quantity of an incompatible pollutant introduced by all major contributing industries would result in a concentration of the pollutant in the influent to the treatment works which would inhibit the performance of the treatment process. In such a case, the municipality would have to supplement the Federal standards.

Pretreatment for removal of compatible pollutants is not required by the Federal pretreatment standards. This is based on the premise that pretreatment facilities should not be required for removal of compatible pollutants as a substitute for adequate municipal waste treatment works. This, however, does not preclude State or local pretreatment requirements for compatible pollutants. Pretreatment of wastewaters containing compatible pollutants may be necessary in the form of spill protection or flow equalization in order to ensure compliance with the Federal pretreatment standards and permitted effluent limitations.

SECTION IV

STATE AND LOCAL PRETREATMENT REQUIREMENTS

10. Objectives

The Act specifically provides for pretreatment requirements established by State or local law not in conflict with the Federal standards in Appendix A. The Federal standards were established on the basis that each publicly owned treatment works may require pretreatment by users, consistent with applicable State or municipal law. The State or local pretreatment requirements can recognize specific factors (such as treatment processes and plant capacities) which would not be national in scope.

11. Pretreatment Information

Pretreatment information has been compiled, in appendices to these guidelines, as a data source to assist municipalities and others in arriving at effective pretreatment requirements to supplement the Federal pretreatment standards for a specific publicly owned treatment works. This subsection describes the information available, how it was developed, and its application.

a. Information on Materials which Inhibit Biological Treatment Processes

The information in Appendix C identifies concentrations of various materials which can inhibit four types of biological treatment processes: activated sludge, trickling filter, anaerobic digestion, and nitrification. This information was derived from data reported in the technical literature. Documented information on this subject is limited, especially for the synergistic effects of many pollutants present in the wastewaters. Caution must be exercised in applying the data to a specific situation. Appendix C should be used as a guide to evaluate when more detailed study is necessary.

In practice, the concentrations of the materials in the influent to the publicly owned treatment works should be determined. Comparison with the concentrations in Appendix C will indicate whether or not there may be problems. If the influent wastewater concentration is close to the inhibitory concentration in Appendix C, then further study may be necessary. The wastewaters must be analyzed to determine the presence of inhibitory materials and their potential impact on treatment plant performance. This includes consideration of intermittent batch discharges, variations in concentration, and background levels already present in the wastewater. When inhibitory material is present, testing the public water supply will provide an indication of a domestic source of the inhibitory material. However, it must be realized that materials of this type can also be added during domestic water usage.

If information is not given in Appendix C concerning a suspected inhibitory material, it may be necessary to obtain additional data. Potential sources of such data include works treating similar wastes or the results of treatability studies.

b. Information on Industrial Wastewater Characteristics and Pretreatment Unit Operations

The information in Appendix D identifies wastewater characteristics and pretreatment unit operations for twenty-two industrial groups. Characteristics which may require pretreatment or are significant to the joint treatment design are indicated. Also, the unit operations which may be necessary to meet the pretreatment requirements are listed. It is emphasized that the listed unit operations are not mandatory. It is anticipated there will be cases when not all unit operations shown will be needed and other cases where additional unit operations will be needed.

For each of sixteen industries in Appendix D a brief summary is provided concerning the nature of the industry, industrial practices, and pretreatment information.

Appendix D groups the industries in terms of Standard Industrial Classification Codes. These codes are as contained in the 1972 edition of the Standard Industrial Classification Manual prepared by the Executive Office of Management and Budget. The Manual is available from the Superintendent of Documents, Government Printing Office, Washington, D. C. 20402. For some industry groups, subgroups with common pretreatment characteristics have been identified.

The following industry groups are included in Appendix D:

- Paper and Allied Products
- Dairy Products
- Textiles
- Seafoods
- Pharmaceuticals
- Leather Tanning and Finishing
- Sugar
- Petroleum Refining
- Meat Products
- Grain Milling
- Fruit and Vegetables
- Beverages
- Plastic and Synthetic Materials
- Blast Furnaces, Steel Works, and Rolling and Finishing
- Organic Chemicals
- Metal Finishing
- Inorganic Fertilizers
- Electric and Steam Generation
- Aluminum
- Flat Glass, Cement, Lime, Concrete Products, Gypsum, and Asbestos
- Inorganic Chemicals
- Industrial Gas Products

The major data sources used to characterize the wastewater include:

(1) Industrial effluent guidance documents developed by EPA.

(2) EPA research reports.

(3) Information in the technical literature.

Most of the data were derived from EPA publications; other sources were used to fill in data gaps. Ranges of different waste constituents present in industrial wastewaters were designated on the basis of a review of the data available.

The following classification system was used to describe the characteristics of industrial wastewaters in relation to domestic wastewaters:

	Classification			
Waste Constituents	Low	Average	High	Extremely High
BOD_5, mg/L	< 200	200-300	300-1,000	$> 1,000$
COD, mg/L	< 300	300-450	450-1,500	$> 1,500$
SS, mg/L	< 200	200-300	300-1,000	$> 1,000$
Temp., °C	< 15	15-25	> 25	-
pH	< 6 (acid)	6-9	> 9 (alkaline)	-

The wastewater characteristics information can be used to identify conditions which should be carefully evaluated when establishing pretreatment requirements for a specific industry and in the design of the joint treatment works. The list of wastewater characteristics can be used as a guideline for developing a wastewater testing program for a particular industry.

For industrial wastewaters from each industry group or pretreatment sub-group, pretreatment unit operations generally considered necessary for three types of municipal secondary treatment processes are identified. These processes are:

1. Suspended biological systems (activated sludge process including modifications, aerated lagoon process).

2. Fixed biological systems (trickling filter and modifications, rotary disc).

3. Independent physical/chemical system (chemical addition, sedimentation, pH adjustment, filtration, carbon adsorption).

Before application of the pretreatment unit operations information, full consideration must be given to Federal pretreatment standards, permit effluent limitations, relative flow ratios, and pollutants which could inhibit biological processes.

12. Pretreatment Ordinance

National requirements for major contributing industries will be controlled under the pretreatment standards (Appendix A). However, it is important that no discharge, from any source, to the publicly owned treatment works cause physical damage, interfere with treatment processes, or result in a violation of effluent limitations. There must, therefore, be a legal basis for regulating and controlling all discharges to the publicly owned treatment works. A municipal ordinance or statute, embodying the pretreatment principles in these guidelines, would meet this requirement. It may be necessary to establish a local system which will allocate waste loads to industrial users so that biological treatment processes are not inhibited and to ensure that effluent limitations are met.

Detailed information and suggested formats are readily available regarding ordinances to regulate the use of sewers and the wastewaters discharged to them. Many States and regional authorities have published instructions or model ordinances. These sources should be consulted for comprehensive information on ordinance preparation. The ordinance should then be adapted to local conditions and to the pretreatment principles in these guidelines.

13. Example Calculations

When the Federal pretreatment standards (Appendix A) govern, industrial users will be able to determine their pretreatment requirements with other information which is publicly available. However, when effluent limitations (such as water quality standards or toxic effluent standards) govern for a particular pollutant, then the pretreatment requirements may have to be made more stringent than the Federal standards, so that effluent limitations are met. In this case, it will be necessary for the municipality to allocate loads of these pollutants which the industry or industries will be permitted to introduce into the municipal system.

There are numerous ways to accomplish waste load allocation. Some large municipalities, where there are many industries of the same type and similar size, specify an allowable pollutant concentration to be met by all users.

Another method would be to allocate waste loads in proportion to the waste load which would be allowable if the Federal pretreatment standards governed. This procedure is illustrated in the following example:

Wastewater flow	8 MGD

Major Contributing Industries:

Industry X

Production	100 tons/day
Wastewater flow	1 MGD

Wastewater contains incompatible pollutant I

Industry Y	
Production	200 tons/day
Wastewater flow	1 MGD
Wastewater contains incompatible pollutant I	

The guidelines for best practicable control technology currently available for pollutant I are:

Industry X	1.0 pounds/ton
Industry Y	1.5 pounds/ton

The Federal pretreatment standards for the major contributing industries would be as follows (the municipality is not committed in its NPDES permit to remove any percentage of the incompatible pollutant I):

Industry X: 100 tons/day × 1.0 pound/ton = 100 pounds/day

Industry Y: 200 tons/day × 1.5 pound/ton = 300 pounds/day

Total 400 pounds/day

However, the municipality makes a determination, based on an evaluation of the permitted effluent limitations for the treatment works, that it can accept a total of only 280 pounds per day of incompatible pollutant I. If the allocation is in proportion to the quantity of pollutant each could have introduced under the Federal pretreatment standards, then:

Pollutant I Allocation to Industry X =

$$\frac{100}{400}\ (280) = 70 \text{ pounds/day}$$

Pollutant I Allocation to Industry Y =

$$\frac{300}{400}\ (280) = 210 \text{ pounds/day}$$

14. Other Considerations

The sample calculations presented in the immediately preceding Subsection show one method for determining waste load allocations. However, in addition to ensuring that the effluent limitations are met, it is necessary to evaluate the industrial wastewaters to ensure that there is no interference with the publicly owned treatment works operation.

Some of the factors to be evaluated are:

a. Conformance with Federal pretreatment standards (Appendix A).

b. Compatibility with the entire treatment works, including sewers, pumping stations, and sludge handling and disposal. Potential for the following types of interference should be considered:

    (1) Severe corrosion damage.

    (2) Significant deposits or abrasion which would substantially reduce the design capacity of sewers and wet wells or which would cause structural collapse.

    (3) Pollutant concentration in sludges such that sludge handling, stabilization, or disposal is adversely affected.

c. Cost-effectiveness of treatment in the publicly owned treatment works compared with pretreatment.

d. Possible presence of materials, in significant concentrations, which could inhibit the treatment process (see Appendix C).

e. Need for pretreatment unit operations discussed in Section IV-Subsection 11 and in Appendix D.

f. Applicability of more stringent State or local pretreatment requirements which govern.

g. Need to conduct treatability studies or test programs to verify findings.

APPENDIX A

federal register

THURSDAY, NOVEMBER 8, 1973
WASHINGTON, D.C.
Volume 38 ■ Number 215

THE NATIONAL ARCHIVES OF THE UNITED STATES
1934

PART III

ENVIRONMENTAL PROTECTION AGENCY

■

WATER PROGRAMS

Pretreatment Standards

Title 40—Protection of the Environment

CHAPTER I—ENVIRONMENTAL PROTECTION AGENCY

SUBCHAPTER D—WATER PROGRAMS

PART 128—PRETREATMENT STANDARDS

On July 19, 1973, notice was published in the FEDERAL REGISTER that the Environmental Protection Agency was proposing standards for pretreatment of pollutants introduced into publicly owned treatment works pursuant to section 307(b) of the Federal Water Pollution Control Act Amendments of 1972 (the Act). Written comments on the proposed rulemaking were invited and received from interested parties and the public. In addition, a public hearing was held in Washington, D.C., on September 26, 1973. The Environmental Protection Agency has carefully considered all comments received and the record of the public hearing. All written comments and a transcript of the public hearing are on file with the Agency. As indicated below, the regulation has been modified in response to some of the comments. The following discussion also outlines the reasons why other suggested changes were not made.

Under section 307(b) of the Act, Federal pretreatment standards are designed to achieve two purposes: (1) To protect the operation of publicly owned treatment works, and (2) to prevent the discharge of pollutants which pass through such works inadequately treated.

Section 128.131 sets forth a number of prohibitions designed to protect the operation of publicly owned treatment works. The prohibitions are self-explanatory. One commenter suggested that § 128.131 is deficient in that it fails to impose specific numerical limitations on the discharge of pollutants that interfere with the operation of publicly owned treatment works. However, the Agency has been unable to formulate such specific numerical limitations. In the first place, the data that are presently available are not considered sufficient to support uniform national standards prescribing permissible concentrations of particular pollutants in publicly owned treatment works. Moreover, the degree that any pollutant interferes with the operation of a publicly owned treatment works depends on the concentration of pollutant in the treatment works itself, rather than the concentration in each user's effluent. But for a national pretreatment standaard to be workable and enforceable, it must prescribe the quality of the user's effluent; otherwise, the user will not know what steps he must take to comply with the standard. It is impossible in a uniform national pretreatment standard to relate the quality of the user's effluent to the concentration of various pollutants in the publicly owned treatment works, since this relationship will vary in each sewer system depending on the quantity of the user's effluent as compared with the quantity of other effluents in the system.

Section 128.133 is based on the premise that pollutants which pass through publicly owned treatment works in amounts greater than would be permitted as a minimum treatment requirement for similar industrial sources discharging directly to navigable waters should be considered adequately treated. The fact that a discharger chooses to use a municipal sewer system, rather than discharging his wastes directly to the navigable waters, should not as a matter of general principle involve a penalty to the environment.

On the basis of this premise, § 128.133 requires users in industrial categories subject to effluent guidelines issued under section 304(b) of the Act, which are discharging incompatible pollutants to publicly owned treatment works, to adopt best practicable control technology currently available, as defined by the Administrator pursuant to section 304 (b) of the Act.

During the public comment period, questions were raised as to whether the effluent limitations guidelines would be appropriate in all cases for application to users of publicly owned treatment works. The Agency recognizes that for some industrial categories it may be necessary to further refine the effluent limitations guidelines to deal with problems that may arise in the application of such guidelines to users of publicly owned treatment works. However, the Agency believes that any adjustments required for particular industrial categories should be considered in connection with the promulgation of the individual effluent guidelines, rather than in the national pretreatment standard. Accordingly, when effluent limitations guidelines are promulgated for individual industrial categories, the Agency will also propose a separate provision for their application to users of publicly owned treatment works. Additional language has been added to § 128.133 to clarify this intent.

It was unclear whether § 128.133 as proposed covered sources that would be new sources if they were discharging directly into the navigable waters. Section 307(c) of the Act requires promulgation of separate pretreatment standards for such sources. Pursuant to section 307(c), the Agency has proposed pretreatment standards for such sources in connection with its proposal of new source performance standards under Section 306 of the Act. Accordingly, § 128.133 has been modified to make it clear that it covers only sources that are not subject to section 307(c) of the Act.

Section 128.133 allows a credit for the percentage removal of an incompatible pollutant to which the publicly owned treatment works is committed in its permit. To insure the basis for allowing such credit, a commitment with respect to a percentage removal of an incompatible pollutant will be included in the permit at the request of a municipality where a basis for such commitment can be demonstrated.

Some commenters suggested that the credit in § 128.133 for removal at the joint treatment works, where there is a commitment to such removal in the NPDES permit, is unrealistic, since municipalities will be unwilling to enter into such commitments. However, in order to achieve the goal of preventing the discharge of incompatible pollutants through municipal systems in amounts greater than the minimum requirements if the discharge were directly into the navigable waters, it is necessary that the required reduction be contained in an enforceable commitment either on the part of the industrial user or the joint treatment works. The industrial user should not be relieved of the commitment to achieve the required degree of reduction except to the extent that the joint treatment works is able to assume a commitment to remove the pollutant.

One commenter suggested that users should be required to comply with toxic effluent standards under section 307(a) of the Act, as well as the requirement of best practicable control technology currently available under section 301(b) and 304(b) of the Act. However, toxic effluent standards will be designed to protect aquatic life in the receiving body of water from both acute and chronic effects. Acute effects will be covered by concentration standards while chronic effects will be covered by weight limitations. Both types of standards will be applicable to the discharge from the publicly owned treatment works. Toxic effluent standards will not be designed to protect sewer systems, and thus it would not be appropriate to apply them to discharges into the system. To the extent that toxic materials in the users' discharges interfere with the operation of publicly owned treatment works, the problem can be otherwise addressed under these standards (§ 128.131) or under local standards using the pretreatment guidelines issued under section 304(f) of the Act. While toxic materials in the users' discharge may appear in the sludge generated by the publicly owned treatment works, the Agency has no basis for making a national determination that the resultant sludge disposal problem is any worse than the problem that would be created if the individual users removed the toxics from their effluent and disposed of the resultant materials individually. This is a factor which must be determined by State and local authorities, taking into account the capabilities of their sludge disposal system and the pollutants present in the wastes from industrial users.

The presence of toxic pollutants in toxic amounts is utilized in the regulation in order to identify "major contributing industries" for purposes of the pretreatment requirements for incompatible pollutants. The purpose here is to identify industrial users whose effluent is significant enough to warrant the imposition of controls based on best practicable control technology currently available without undue administrative burden, rather than to indicate that it is appropriate to impose toxic effluent standards on industrial users.

The definition of "compatible pollutant" has been broadened to recognize the fact that some joint treatment works are designed to achieve substantial removal of pollutants other than the four pollutants listed in the definition in the proposed regulation (BOD, suspended solids, pH, and fecal coliform bacteria). Where the joint treatment works was designed to and does achieve substantial removal of a pollutant, it is not appropriate to require the industrial user to achieve best practicable control technology currently available, since this would lead to an uneconomical duplication of treatment facilities. While the term "substantial removal" is not subject to precise definition, it generally contemplates removals in the order of 80 percent or greater. Minor incidental removals in the order of 10 to 30 percent are not considered "substantial".

There was a diversity of comments on the length of the time for compliance and its relation to the promulgation of the definition of best practicable control technology currently available. The Act requires that pretreatment must specify a time for compliance not to exceed three years from the date of promulgation. The Agency has concluded that a period not greater than three years from the date of promulgation is appropriate for compliance for § 128.131. For Section 128.133 the same period is also considered an appropriate time for compliance. However, the standard set forth in § 128.133 will not be complete until promulgation of the separate provision, as required by Section 128.133, setting forth the application to pretreatment of the effluent limitations guideline for a given industrial category.

Accordingly, § 128.140 provides that the period of compliance with § 128.133 will not commence for any particular category of user until promulgation of that separate provision. Section 128.140 has been further modified to establish an interim requirement for commencement of construction, and a requirement for compliance reports. It was concluded that without such requirements, timely compliance with the pretreatment standard might be unenforceable as a practical matter.

Some commenters questioned the need for these pretreatment standards or the relationship between these standards and local pretreatment programs. It is important to note the clear requirements in the Act that there be both national pretreatment standards, Federally enforceable, and EPA pretreatment guidelines to assist States and municipalities in developing local pretreatment programs. The Agency recognizes that in some cases, these pretreatment standards may not be sufficient to protect the operation of a publicly owned treatment works or to enable the treatment works to comply with the terms of its NPDES permit. This may be the case, for example, when the terms of the permit for the publicly owned treatment works are dictated by water quality standards or toxic standards. In such cases, the State or municipality may have to impose more stringent pretreatment standards under State or local laws than are specified in these regulations to enable compliance with NPDES permits issued to publicly owned treatment works. The agency considers it essential that such local pretreatment requirements be established for each system where necessary to ensure compliance with the NPDES permit.

Pretreatment guidelines will be published, pursuant to section 304(f) of the Act, to assist the States and municipalities in establishing their own pretreatment requirements.

Effective date. This regulation will become effective December 10, 1973.

JOHN QUARLES,
Acting Administrator.

NOVEMBER 1, 1973.

NOTE.—The EPA pamphlet, Pretreatment of Discharges to Publicly Owned Treatment Work, is filed as part of the original document.

Sec.
128.100 Purpose.
128.101 Applicability.
128.110 State or local law.
128.120 Definitions.
128.121 Compatible pollutant.
128.122 Incompatible pollutant.
128.123 Joint treatment works.
128.124 Major contributing industry.
128.125 Pretreatment.
128.130 Pretreatment standards.
128.131 Prohibited wastes.
128.132 Pretreatment for compatible pollutants.
128.133 Pretreatment for incompatible pollutants.
128.140 Time for compliance.

AUTHORITY: Sec. 307(b) Pub. L. 92-500; 86 Stat. 857 (33 U.S.C. 1317).

§ 128.100 Purpose.

The provisions of this part implement section 307(b) of the Federal Water Pollution Control Act Amendments of 1972 (Public Law 92-500) hereinafter referred to as "the Act".

§ 128.101 Applicability.

The standards set forth in § 128.131 apply to all non-domestic users of publicly owned treatment works. The standard set forth in § 128.133 applies only to major contributing industries.

§ 128.110 State or local law.

Nothing in this part shall affect any pretreatment requirement established by any State or local law not in conflict with any standard established pursuant to this Part. In particular cases, a State or municipality, in order to meet the effluent limitations in a NPDES permit for a publicly owned treatment works may find it necessary to impose pretreatment requirements stricter than those contained herein.

§ 128.120 Definitions.

Definitions of terms used in this part are as follows:

§ 128.121 Compatible pollutant

For purposes of establishing Federal requirements for pretreatment, the term "compatible pollutant" means biochemical oxygen demand, suspended solids, pH and fecal coliform bacteria, plus additional pollutants identified in the NPDES permit if the publicly owned treatment works was designed to treat such pollutants, and in fact does remove such pollutants to a substantial degree. Examples of such additional pollutants may include:

Chemical oxygen demand.
Total organic carbon.
Phosphorus and phosphorus compounds.
Nitrogen and nitrogen compounds.
Fats, oils, and greases of animal or vegetable origin except as prohibited under § 128.131(c).

§ 128.122 Incompatible pollutant.

The term "incompatible pollutant" means any pollutant which is not a compatible pollutant as defined in § 128.121.

§ 128.123 Joint treatment works.

Publicly owned treatment works for both non-industrial and industrial wastewater.

§ 128.124 Major contributing industry.

A major contributing industry is an industrial user of the publicly owned treatment works that; (a) Has a flow of 50,000 gallons or more per average work day; (b) has a flow greater than five percent of the flow carried by the municipal system receiving the waste; (c) has in its waste, a toxic pollutant in toxic amounts as defined in standards issued under section 307(a) of the Act; or (d) is found by the permit issuance authority, in connection with the issuance of an NPDES permit to the publicly owned treatment works receiving the waste, to have significant impact, either singly or in combination with other contributing industries, on that treatment works or upon the quality of effluent from that treatment works.

§ 128.125 Pretreatment.

Treatment of wastewaters from sources before introduction into the joint treatment works.

§ 128.130 Pretreatment standards.

The following sections set forth pretreatment standards for pollutants introduced into publicly owned treatment works.

§ 128.131 Prohibited wastes.

No waste introduced into a publicly owned treatment works shall interfere with the operation or performance of the works. Specifically, the following wastes shall not be introduced into the publicly owned treatment works:

(a) Wastes which create a fire or explosion hazard in the publicly owned treatment works.

(b) Wastes which will cause corrosive structural damage to treatment works, but in no case wastes with a pH lower than 5.0, unless the works is designed to accommodate such wastes.

(c) Solid or viscous wastes in amounts which would cause obstruction to the flow in sewers, or other interference with the proper operation of the publicly owned treatment works.

(d) Wastes at a flow rate and/or pollutant discharge rate which is excessive over relatively short time periods so that there is a treatment process upset and subsequent loss of treatment efficiency.

§ 128.132 Pretreatment for compatible pollutants.

Except as required by § 128.131, pretreatment for removal of compatible pollutants is not required by these regulations. However, States and municipalities may require such pretreatment pursuant to section 307(b)(4) of the Act.

§ 128.133 Pretreatment for incompatible pollutants.

In addition to the prohibitions set forth in § 128.131, the pretreatment standard for incompatible pollutants introduced into a publicly owned treatment works by a major contributing industry not subject to section 307(c) of the Act shall be, for sources within the corresponding industrial or commercial category, that established by a promulgated effluent limitations guideline defining best practicable control technology currently available pursuant to sections 301(b) and 304(b) of the Act: *Provided*, That, if the publicly owned treatment works which receives the pollutants is committed, in its NPDES permit, to remove a specified percentage of any incompatible pollutant, the pretreatment standard applicable to users of such treatment works shall be correspondingly reduced for that pollutant; and provided further that when the effluent limitations guideline for each industry category is promulgated, a separate provision will be proposed concerning the application of such guideline to pretreatment.

§ 128.140 Time for compliance.

(a) Any owner or operator of any source to which the pretreatment standards required by this Part are applicable, shall be in compliance with such standards within the shortest reasonable time but not later than three years from the date of their promulgation; except that for § 128.133, the three year compliance period for any user shall commence with the date of promulgation of a provision, as required by § 128.133, setting forth the application to pretreatment of the effluent limitations guidelines for the applicable industrial category.

(b) In order to ensure such compliance, each such owner or operator shall commence construction of any required pretreatment facilities within 18 months from the date of final promulgation of the provision required by § 128.133, setting forth the application to pretreatment of the effluent limitations guidelines. By the time construction is required to be commenced, each such owner or operator shall furnish to the Regional Administrator (or to any State agency with an approved NPDES permit program) a report, on a form to be prescribed by the Administrator, which shall set forth the effluent limits to be achieved by such pretreatment facilities and a schedule for the achievement of compliance with such limits by the required date. A copy of such report shall be furnished to the municipality or agency operating the publicly owned treatment works into which such pollutants are discharged. Thereafter, each such owner or operator shall furnish the Regional Administrator or his designee with such additional information or reports (including information relating to compliance with effluent limits and schedules for completion of pretreatment facilities) as he may request.

(c) Nothing contained herein shall prevent any municipality or other agency from requiring more stringent pretreatment standards or a more stringent compliance schedule, than as set forth in this part.

[FR Doc.73-23578 Filed 11-7-73;8:45 am]

APPENDIX B

federal register

FRIDAY, AUGUST 17, 1973
WASHINGTON, D.C.

Volume 38 ■ Number 159

PART II

ENVIRONMENTAL PROTECTION AGENCY

■

WATER PROGRAMS

Secondary Treatment Information

Title 40—Protection of Environment

CHAPTER I—ENVIRONMENTAL PROTECTION AGENCY

SUBCHAPTER D—WATER PROGRAMS

PART 133—SECONDARY TREATMENT INFORMATION

On April 30, 1973, notice was published in the FEDERAL REGISTER that the Environmental Protection Agency was proposing information on secondary treatment pursuant to section 304(d)(1) of the Federal Water Pollution Control Act Amendments of 1972 (the Act). Reference should be made to the preamble of the proposed rulemaking for a description of the purposes and intended use of the regulation.

Written comments on the proposed rulemaking were invited and received from interested parties. The Environmental Protection Agency has carefully considered all comments received. All written comments are on file with the Agency.

The regulation has been reorganized and rewritten to improve clarity. Major changes that were made as a result of comments received are summarized below:

(a) The terms "1-week" and "1-month" as used in § 133.102 (a) and (b) of the proposed rulemaking have been changed to 7 consecutive days and 30 consecutive days respectively (See § 133.102 (a), (b), and (c)).

(b) Some comments indicated that the proposed rulemaking appeared to require 85 percent removal of biochemical oxygen demand and suspended solids only in cases when a treatment works would treat a substantial portion of extremely high strength industrial waste (See § 133.102(g) of the proposed rulemaking). The intent was that in no case should the percentage removal of biochemical oxygen demand and suspended solids in a 30 day period be less than 85 percent. This has been clarified in the regulation. In addition, it has been expressed as percent remaining rather than percent removal calculated using the arithmetic means of the values for influent and effluent samples collected in a 30 day period (See § 133.102(a) and (b)).

(c) Comments were made as to the difficulty of achieving 85 percent removal of biochemical oxygen demand and suspended solids during wet weather for treatment works receiving flows from combined sewer systems. Recognizing this, a paragraph was added which will allow waiver or adjustment of that requirement on a case-by-case basis (See § 133.103(a)).

(d) The definition of a 24-hour composite sample (See § 133.102(c) of the proposed rulemaking) was deleted from the regulation. The sampling requirements for publicly owned treatment works will be established in guidelines issued pursuant to sections 304(g) and 402 of the Act.

(e) In § 133.103 of the proposed rulemaking, it was recognized that secondary treatment processes are subject to upsets over which little or no control may be exercised. This provision has been deleted. It is no longer considered necessary in this regulation since procedures for notice and review of upset incidents will be included in discharge permits issued pursuant to section 402 of the Act.

(f) Paragraph (f) of § 133.102 of the proposed rulemaking, which relates to treatment works which receive substantial portions of high strength industrial wastes, has been rewritten for clarity. In addition, a provision has been added which limits the use of the upwards adjustment provision to only those cases in which the flow or loading from an industry category exceeds 10 percent of the design flow or loading of the treatment works. This intended to reduce or eliminate the administrative burden which would be involved in making insignificant adjustments in the biochemical oxygen demand and suspended solids criteria (See § 133.103(b)).

The major comments for which changes were not made are discussed below:

(a) Comments were received which recommended that the regulation be written to allow effluent limitations to be based on the treatment necessary to meet water quality standards. No change has been made in the regulations because the Act and its legislative history clearly show that the regulation is to be based on the capabilities of secondary treatment technology and not ambient water quality effects.

(b) A number of comments were received which pointed out that waste stabilization ponds alone are not generally capable of achieving the proposed effluent quality in terms of suspended solids and fecal coliform bacteria. A few commenters expressed the opposite view. The Agency is of the opinion that with proper design (including solids separation processes and disinfection in some cases) and operation, the level of effluent quality specified can be achieved with waste stabilization ponds. A technical bulletin will be published in the near future which will provide guidance on the design and operation of waste stabilization ponds.

(c) Disinfection must be employed in order to achieve the fecal coliform bacteria levels specified. A few commenters argued that disinfectant is not a secondary treatment process and therefore the fecal coliform bacteria requirements should be deleted. No changes were made because disinfection is considered by the Agency to be an important element of secondary treatment which is necessary for protection of public health (See § 133.102(c)).

Effective date. These regulations shall become effective on August 17, 1973.

JOHN QUARLES,
Acting Administrator

AUGUST 14, 1973.

Chapter I of title 40 of the Code of Federal Regulations is amended by adding a new Part 133 as follows:

Sec.
133.100 Purpose.
133.101 Authority.
133.102 Secondary treatment.
133.103 Special considerations.
133.104 Sampling and test procedures.

AUTHORITY: Secs. 304()(1), 301(b)(1)(B), Federal Water Pollution Control Act Amendments, 1972, P.L. 92-500.

§ 133.100 Purpose.

This part provides information on the level of effluent quality attainable through the application of secondary treatment.

§ 133.101 Authority.

The information contained in this Part is provided pursuant to sections 304(d)(1) and 301(b)(1)(B) of the Federal Water Pollution Control Act Amendments of 1972, PL 92-500 (the Act).

§ 133.102 Secondary treatment.

The following paragraphs describe the minimum level of effluent quality attainable by secondary treatment in terms of the parameters biochemical oxygen demand, suspended solids, fecal coliform bacteria and pH. All requirements for each parameter shall be achieved except as provided for in § 133.103.

(a) *Biochemical oxygen demand (five-day).* (1) The arithmetic mean of the values for effluent samples collected in a period of 30 consecutive days shall not exceed 30 milligrams per liter.

(2) The arithmetic mean of the values for effluent samples collected in a period of seven consecutive days shall not exceed 45 milligrams per liter.

(3) The arithmetic mean of the values for effluent samples collected in a period of 30 consecutive days shall not exceed 15 percent of the arithmetic mean of the values for influent samples collected at approximately the same times during the same period (85 percent removal).

(b) *Suspended solids.* (1) The arithmetic mean of the values for effluent samples collected in a period of 30 consecutive days shall not exceed 30 milligrams per liter.

(2) The arithmetic mean of the values for effluent samples collected in a period of seven consecutive days shall not exceed 45 milligrams per liter.

(3) The arithmetic mean of the values for effluent samples collected in a period of 30 consecutive days shall not exceed 15 percent of the arithmetic mean of the values for influent samples collected at approximately the same times during the same period (85 percent removal).

(c) *Fecal coliform bacteria.* (1) The geometric mean of the value for effluent samples collected in a period of 30 consecutive days shall not exceed 200 per 100 milliliters.

(2) The geometric mean of the values for effluent samples collected in a period of seven consecutive days shall not exceed 400 per 100 milliliters.

(d) *pH*. The effluent values for pH shall remain within the limits of 6.0 to 9.0.

§ 133.103 Special considerations.

(a) *Combined sewers*. Secondary treatment may not be capable of meeting the percentage removal requirements of paragraphs (a)(3) and (b)(3) of § 133.102 during wet weather in treatment works which receive flows from combined sewers (sewers which are designed to transport both storm water and sanitary sewage). For such treatment works, the decision must be made on a case-by-case basis as to whether any attainable percentage removal level can be defined, and if so, what that level should be.

(b) *Industrial wastes*. For certain industrial categories, the discharge to navigable waters of biochemical oxygen demand and suspended solids permitted under sections 301(b)(1)(A)(i) or 306 of the Act may be less stringent than the values given in paragraphs (a)(1), and (b)(1) of § 133.102. In cases when wastes would be introduced from such an industrial category into a publicly owned treatment works, the values for biochemical oxygen demand and suspended solids in paragraphs (a)(1) and (b)(1) of § 133.102 may be adjusted upwards provided that: (1) the permitted discharge of such pollutants, attributable to the industrial category, would not be greater than that which would be permitted under sections 301(b)(1)(a)(i) or 306 of the Act if such industrial category were to discharge directly into the navigable waters, and (2) the flow or loading of such pollutants introduced by the industrial category exceeds 10 percent of the design flow or loading of the publicly owned treatment works. When such an adjustment is made, the values for biochemical oxygen demand or suspended solids in paragraphs (a)(2) and (b)(2) of § 133.102 should be adjusted proportionally.

§ 133.104 Sampling and test procedures.

(a) Sampling and test procedures for pollutants listed in § 133.102 shall be in accordance with guidelines promulgated by the Administrator pursuant to sections 304(g) and 402 of the Act.

(b) Chemical oxygen demand (COD) or total organic carbon (TOC) may be substituted for biochemical oxygen demand (BOD) when a long-term BOD:COD or BOD:TOC correlation has been demonstrated.

[FR Doc.73-17194 Filed 8-16-73;8:45 am]

Appendix C

Information on Materials which Inhibit Biological Treatment Processes

The following paragraphs comprise a discussion of the sources of information on various materials, which inhibit biological treatment systems, presented in this Appendix.

Copper

Rudolfs (1) has indicated that copper in raw sewage at 1 mg/L either inhibited or retarded the aerobic metabolism. Barth, et al (2), and McDermott, et al (3) have shown, from pilot-plant studies, that continuous addition of 1.0 mg/L of copper is the threshold value for activated sludge. The maximum concentration of copper that can be received continuously without having a detectable effect on common parameters for effluent quality is 1.0 mg/L (3). Where there is concern about turbidity, a concentration of 0.8 mg/L of copper appears to be the upper limit beyond which an effluent on pilot-plant studies conducted with copper sulfate and copper-cyanide complex additions.

When four-hour slug doses of copper were added to the activated sludge system, the performance was affected when the copper concentration in the feed approached 75 mg/L (2,3,4). The same studies have indicated that heavy metals present in sewage (whether alone or in combination) affected the nitrification process and that no acclimation was possible. Kalabina, et al (5) have indicated that copper fed as copper sulfate inhibited nitrification when the concentration of copper exceeded 0.5 mg/L. They also recommended a copper concentration of less than 0.1 mg/L in raw sewage for biological treatment.

With respect to anaerobic digestion, a copper concentration of 10 mg/L in raw sewage affected gas production in the digestion of primary sludge (2). When anaerobic digestion of combined primary and secondary sludges was involved, a copper concentration of 5 mg/L in raw sewage affected the digestion process (2). However, other reports indicated that copper concentrations in the range of 0.2 mg/L to 2.5 mg/L in raw sewage were deleterious to the anaerobic digestion process (1,5).

Zinc

McDermott, et al (6) and Barth, et al (2), have shown from pilot-plant studies that zinc (either in the form of $ZnSO_4$ or in the form found in a typical alkaline cyanide plating bath) added to raw sewage produced similar effects on biological systems. The maximum level of zinc that will not produce a significant effect on treatment efficiency was indicated as being between 2.5 and 10 mg/L when continuously added to the biological system.

When zinc at a concentration of 160 mg/L was added as a slug dose over a four-hour period, a serious reduction in treatment efficiency was observed. The same authors have shown that the anaerobic digestion process was retarded when the zinc concentration in raw sewage reached 20 mg/L. This concentration is in agreement with those reported by Rudolfs (1). Other investigators have indicated a maximum concentration of 5 mg/L Zn in raw sewage to prevent decrease in gas production in the anaerobic digestion process (7,8).

Zinc concentrations of approximately 0.5 mg/L in raw sewage have been reported to inhibit nitrification process (9).

Lead

Rudolfs (1) has indicated that lead in raw sewage at concentrations of about 0.1 mg/L will inhibit or retard the aerobic biological metabolism. This is in agreement with the values reported by Kalabina from studies conducted using lead sulfate (5).

Kalabina also studied the effects of lead on nitrification process and showed that 0.5 mg/L of lead in raw sewage inhibited the nitrification process (5).

Cadmium

Mosey (10,11) reported that cadmium ions, added to experimental digesters, have a threshold value (for adverse effect on biologic treatment processes) of 0.02 mg/L and occurs at a carbonate ion concentration of 2×10^{-5} moles/L. The results also showed that the toxicity of cadmium to anaerobic digestion was pH-dependent when the pH was greater than 7.0 and independent of the pH when the pH was less than 7.0.

The foregoing results were based on laboratory studies, and the cadmium concentrations refer only to those present in the digester.

Boron and Arsenic

Banerji, et al (12) studied the effects of boron added in slug doses to activated sludge treatment. The results indicated that a slug dosage of 10 mg/L in raw waste adversely affected the performance of aerobic metabolism. However, Rudolfs (1) indicated that boron in raw sewage affected the performance of activated sludge and trickling filters at much lower levels (1.0 mg/L and less). He also indicated that the addition of arsenic at concentrations of approximately 4 mg/L to digesting sludge inhibited or retarded the performance of digesters.

Chromium

Rudolfs (1) indicated that chromium was toxic to activated sludge and trickling filter processes when the raw sewage contained 3 mg/L total chromium. It was pointed out that when the total chromium in raw sewage was in the range of 1-5 mg/L, the anaerobic digestion process was significantly retarded.

However, the pilot-plant results of Barth, et al (2) indicate that a continuous dosage of 10 mg/L of chromate chromium was required before the aerobic process deteriorated. With respect to slug dosage, the activated sludge pilot-plant was able to withstand up to 500 mg/L of chromate chromium when applied over a four-hour period (13). Their studies also showed that the anaerobic digestion process was affected when the hexavalent chromium in raw sewage exceeded 50 mg/L. These values were significantly higher than those reported by Rudolfs (1). According to Rudolfs, hexavalent chromium concentrations at 1.0 mg/L in raw sewage affected trickling filter process, and at the 1-50 mg/L level the anaerobic digestion process was affected.

It is important to point out here that the toxicity of heavy metals on biological systems is closely associated with sulfate concentrations in raw wastewater and therefore should not be compared directly with one another without considering the concentration of the sulfate ion. Unfortunately, the studies did not report the sulfate concentrations necessary for making such a comparison.

With respect to the nitrification process, Whiteland, et al (14) have reported that the nitrification process was severely affected when the hexavalent chromium in raw sewage was in the range of 2 to 5 mg/L.

Nickel

Pilot-plant studies conducted with continuous addition of $NiSO_4$ in raw sewage indicated that nickel concentrations at 2.5, 5, and 10 mg/L affected both biological treatment efficiency and effluent clarity (15). The results indicated that nickel doses of 1 mg/L on a continuous basis can be tolerated by aerobic biological processes. However, it is important to point out that most of the nickel reaching the aeration process passed through the effluent in soluble form (2,3). These results also indicated that the anaerobic digestion process was very resistant to nickel in the sludges. Primary sludges containing up to 40 mg/L of nickel digested satisfactorily.

However, other reports indicate (8) that nickel concentrations of 2 mg/L in raw sewage would be inhibitory to the anaerobic digestion process. In addition, the nitrification process will be severely inhibited when the nickel concentration is approximately 0.5 mg/L (9).

Cyanides

Coburn (16) reported that 5 mg/L of cyanide in raw wastewater (discharging continuously) interfered with activated sludge treatment. In trickling filter studies, cyanide in raw sewage at 30 mg/L produced poor effluent quality. However, when the cyanide concentration was only 10 mg/L, 98 to 100 percent of the cyanide was destroyed in the trickling filter (7). These levels are higher than those reported by Rudolfs (1). According to Rudolfs, 1 to 2.0 mg/L of cyanide (as HCN) in raw sewage affected the performance of the activated sludge, trickling filters, and anaerobic digestion processes (1,16). Generally, however, secondary biological treatment processes can oxidize the cyanide if acclimatized (17). Rudolfs (1) has also reported that the nitrification process was inhibited when the cyanide (HCN) concentration in raw sewage reached 2 mg/L.

Sulfides and Sulfates

Pohland and Kang (18) reported in their review of literature on anaerobic processes that when the sulfate concentration exceeded 500 mg/L, the gas production was greatly reduced. Similar results were also reported indicating that sulfate concentrations of 300 mg/L are toxic to anaerobic digestion. The sulfate toxicity was related to the reduction to sulfides during digestion (17).

Lawrence, et al (19) and Rudolfs (20) have reported that sulfide concentrations in the range of 150-200 mg/L in the digester feed would reduce gasification considerably.

Ammonia

Drague, et al (21) reported that ammonia concentrations in the range of 1,500-3,000 mg/L inhibited the anaerobic digestion process. When the ammonia concentration reached 3,000 mg/L, the feed sludge became strongly toxic to the digestion process.

This is in agreement with the values reported by Rudolfs (1). The concentration of ammonia refers to that present in the influent to the digesters of accumulated in the digesters.

Sodium Chloride

The presence of sodium chloride in raw sewage or in the digester has been reported to produce deleterious effects both in aerobic biological systems and in anaerobic digesters. Rudolfs has indicated that the gas production in anaerobic digestion will be greatly reduced when the NaCl concentration reaches 50,000 mg/L in digesters (1). Studies conducted by Kincannon (22) indicated that the laboratory-scale aerobic biological system was greatly affected at NaCl concentrations of 10,000 mg/L in raw wastewater. Similar results were reported by Lawton and Eggert (23) in the case of trickling filters.

Chloroform

Ghosh (11), in a review of the anaerobic digestion process literature, reported that chloroform addition to digesters on a continuous basis produced noticeable effects at a concentration of 10 to 11 mg/L. When chloroform application was as a slug dosage. the anaerobic process was adversely affected at 1 mg/L concentration in the feed.

Free Oil

Free oil of petroleum origin, at concentrations in the range of 50-100 mg/L, has been reported as interfering with aerobic biological treatment (24,25). The oil concentrations were measured according to the API Manual using CCl_4 extraction (26). The measurement of free oil using the API procedure may also include oily materials of animal and vegetable origin.

Other Cations (Na^+, K^+, Ca^+, and Mg^{++})

Malina (27) has presented data on the effects of several cations on anaerobic digestion. The results indicated that: Ca^{++} strongly inhibited anaerobic digestion at a concentration of 8,000 mg/L; Mg^{++} at a concentration of 2,000 mg/L; K^+ at 12,000 mg/L; and Na^+ at 8,000 mg/L. These results were in close agreement with those reported by Kugelman and McCarty (28).

Chlorinated Organic Compounds

The effect of several chlorinated organic compounds, at very low concentrations, on anaerobic digestion of biological sludges is marked, and constitutes a warning that a close watch must be kept on the disposal of these compounds. Jackson, et al (29) have summarized the results on toxicity of various chlorinated organic compounds, as indicated in Table C-1. These results indicate that chlorinated compounds can be toxic to anaerobic digestion at levels varying between 0.1 to 20 mg/L. The degree of inhibition will depend on the particular chemical itself. Further studies are required to determine the long-term effects of chlorinated organic compounds on municipal biological treatment processes when they are present separately or in various combinations.

REFERENCES

1. Rudolfs, W., "Review of Literature on Toxic Materials Affecting Sewage Treatment Processes, Streams, and BOD Determinations", Sewage and Industrial Wastes, 22, 9, 1157-1191 (1950).

2. Barth, E.B., et al, "Summary Report on the Effects of Heavy Metals on the Biological Treatment Processes", Journal WPCF, 37, 1, 86-96 (1965).

3. "Interaction of Heavy Metals and Biological Sewage Treatment Processes", Public Health Service Publication No. 999-WP-22, U.S. Dept. of Health, Education and Welfare, Cincinnati, Ohio (May, 1965).

4. McDermott, G.N.,et al, "Copper and Anaerobic Sludge Digestion", Journal WPCF, 35, 5, 655-662 (1963).

5. Kalabina, M., et al. "Effect of Copper and Lead Bearing Wastes on the Purification of Sewage", Water and Sewage Works, 93, 1, 30 (1946).

6. McDermott, G.N., et al, "Zinc in Relation to Activated Sludge and Anaerobic Digestion", Proc. 17th Industrial Waste Conference, Purdue University, Rafayette, Ind., 461-475 (1962).

7. "The Effect of Industrial Wastes on Sewage Treatment", Publication No. TR-13, New England Interstate Water Pollution Control Commission, Boston, Mass. (1965).

8. Nemerow, N.L., "Theories and Practices of Industrial Waste Treatment", Addison-Wiley Publishing Company, Reading, Mass. (1963).

9. Air and Water News, 5, 40, 8-9 (October 11, 1971).

10. Mosey, F.E., "The Toxicity of Cadmium to Anaerobic Digestion: Its Modification by Inorganic Ions", Water Pollution Control (G-B), 70, Part 5, 584-598 (1971).

11. Ghosh, S., "Anaerobic Processes - Literature Review", Journal WPCF, 44, 6, 948-959 (1972).

12. Banerji, S.K., et al. "Effect of Boron on Aerobic Biological Waste Treatment", Proc. 23rd Industrial Waste Conference, Purdue University, Lafayette, Ind., 956-965 (1968).

13. Moore, W.A., et al, "Effects of Chromium on the Activated Sludge Process", Journal WPCF, 33, 1, 54-72 (1961).

14. Whiteland, A.B., et al, "Pilot Plant Experiments on the Effects of Some Constituents of Industrial Wastewaters on Sewage Treatment", Water Pollution Control (G-B), 70, 626-643 (1971).

15. McDermott, G.N., et al, "Nickel in Relation to Activated Sludge and Anaerobic Digestion Processes", Journal WPCF, 37, 2, 163-177 (1965).

16. Coburn, S.E., "Limits for Toxic Wastes in Sewage Treatment", *Jour. Sew. Works*, *21*, 3, 522-524 (1949).

17. "Controlling the Effects of Industrial Wastes on Sewage Treatment", Publication No. TR-15, New England Interstate Water Pollution Control Commission, Boston, Mass. (1971).

18. Pohland, F.G., and Kang, S.J., "Anaerobic Processes - Literature Review," *Jour. WPCF*, *43*, 6, 1129-1134 (1971).

19. Lawrence, A.W., et al, "The Effects of Sulfide on Anaerobic Treatment," *Proc. 19th Ind. Waste Conf.*, Purdue University, Lafayette, Ind., 343-357 (1964).

20. Rudolfs, W., and Amberg, H.R., "White Water Treatment, II. Effect of Sulfides on Digestion." *Sew. and Ind. Wastes*, *24*, 10, 1278-1287 (1952).

21. Dague, R.R., et al, "Digestion Fundamentals Applied to Digester Recovery - Two Case Studies." *Jour. WPCF*, *42*, 9, 1666-1675 (1970).

22. Kincannon, D.F., "Studies on the Effects of Sodium Chloride on Activated Sludge." Ph.D. Thesis, Oklahoma State University, Stillwater, Okla. (1965).

23. Lawton, G.W., and Eggert, C.V., "Effect of High Sodium Chloride Concentration on Trickling Filter Slimes." *Jour. WPCF*, *29*, 11, 1228-1242 (1957).

24. Beychok, M.R., "*Aqueous Wastes from Petroleum and Petrochemical Plants*." John Wiley & Sons, New York (1967).

25. "Manual on Disposal of Refinery Wastes," Volume on Liquid Wastes, American Petroleum Institute, New York (1969).

26. "Manual on Disposal of Refinery Wastes," Vol. IV - "Sampling and Analysis of Wastewater," American Petroleum Institute, New York (1957).

27. Malina, J.F., "Anaerobic Waste Treatment," Unpublished Report.

28. Kugelman, I.J., and McCarty, P.L., "Cation Toxicity and Stimulation in Anaerobic Waste Treatment - II. Daily Feed Studies," *Proc. 19th Ind. Waste Conference*, Purdue University, Lafayette, Ind., 667-686 (1964).

29. Jackson, S., Phil, D., and Brown, V. M., "Effect of Toxic Wastes on Treatment Processes and Watercourses." Proceedings of the Annual Conference, The Institute of Water Pollution Control, Douglas, Isle of Man, England (1969).

30. McCarty, P. L., "Anaerobic Waste Treatment Fundamentals; Part 3, Toxic Materials and Their Control." Jour. Public Works (Nov. 1964).

31. Wheatland, A. B., Bell, M. G. W., and Atkinson, A., "Pilot Plant Experiments on the Effects of Some Constituents of Industrial Waste Waters on Sewage Treatment." Jour. Inst. of Sew. Purif., No. 6 (1971).

32. Pettet, A. E. J., and Mills, E. V., "Biological Treatment of Cyanide with and without Sewage." Jour. Appl. Chem., 4 (Aug. 1954).

Table C-1

Information on Materials Which Inhibit Biological Treatment Processes

Pollutant	Aerobic Processes	Anaerobic Digestion	Nitrification	References
	Concentration[1], mg/L			
Copper	1.0	1.0	0.5	(1)(2)(3)(4)(5)(16)
Zinc	5.0	5.0	0.5	(2)(6)(7)(8)(9)
Chromium (Hexavalent)	2.0	5.0	2.0	(1)(2)(13)(14)
Chromium (Trivalent)	2.0	2000[2]	*	(1)
Total Chromium	5.0	5.0	*	(1)
Nickel	1.0	2.0	0.5	(1)(8)(9)(15)
Lead	0.1	*	0.5	(1)(5)(29)
Boron	1.0	*	*	(1)(12)
Cadmium	*	0.02[2]	*	(10)
Silver	0.03	*	*	(29)
Vanadium	10	*	*	(29)
Sulfides (S^{-})	*	100[2]	*	(10)(19)(20)
Sulfates (SO_4^{-})	*	500	*	(10)(17)(18)(19)(20)
Ammonia	*	1500[2]	*	(17)(18)(30)
Sodium (Na^{+})	*	3500	*	(27)(28)(30)
Potassium (K^{+})	*	2500	*	(27)(28)(30)
Calcium (Ca^{++})	*	2500	*	(27)(28)(30)
Magnesium (Mg^{++})	*	1000	*	(27)(28)(30)
Acrylonitrite	*	5.0[2]	*	(29)
Benzene	*	50[2]	*	(29)
Carbon Tetrachloride	*	10[2]	*	(29)
Chloroform	18.0	0.1[2]	*	(29)
Methylene Chloride	*	1.0	*	(29)
Peintachlorophenol	*	0.4	*	(29)
1,1,1-Trichloroethane	*	1.0[2]	*	(29)
Trichlorofluoromethane	*	0.7	*	(29)
Trichlorotrifluoroethane	*	5.0[2]	*	(29)
Cyanide (HCN)	*	1.0	2.0	(1) (16) (17)
Total oil (Petroleum origin)	50	50	50	(24) (25) (26)

* Insufficient data

[1] Concentrations refer to those present in raw wastewater unless otherwise indicated.

[2] Concentrations apply to the digester influent only. Lower values may be required for protection of other treatment process units.

[3] Petroleum-based oil concentration measured according to the API Method 733-58 for determing volatile and non-volatile oily materials. The inhibitory level does not apply to oil of direct animal or vegetable origin.

PAPER AND ALLIED PRODUCTS

1. Industry Description

This industry includes Standard Industrial Classifications (SIC) 2610, 2620, 2630, 2640, 2650, and 2660. These classifications include the manufacture of pulp from wood, rag, and other cellulose fibers and the manufacture of paper, paperboard, and building products. The manufacture of converted paper and paperboard products from purchased paper is not included since it involves a relatively dry process, whose wastewater flows and loadings are not significant to the design of municipal systems. Therefore, the plants making converted paper and paperboard products are excluded.

The manufacture of paper and allied products involves the preparation of wood and other raw materials, separation and recovery of cellulose fibers, and blending of the fibers with proper additives to produce "furnish", which is formed into paper. The additives include: sizing materials such as alum and resins, sodium aluminate, and wax emulsions; synthetics, such as acrylics, isocyanates, and fluocarbons; and fillers such as clays, calcium carbonate and sulfate, talc, barium sulfate, aluminum compounds, and titanium oxide. When fillers are used, retention aids (starches or synthetic resins) are added to increase the retention of the filler.

The principal operations involved in the manufacture of pulp and paper are:

Wood Preparation
Pulping (mechanical, chemical, semi-chemical, and deinking)
Pulp Washing and Screening
Stock Preparation
Paper Making

The pretreatment sub-groups for this industry are as follows:

Integrated pulp and paper mills using mechanical pulping processes (bleached and unbleached)

Integrated pulp and paper mills using chemical pulping processes (unbleached)

Integrated pulp and paper mills using chemical pulping processes (bleached)

Integrated pulp and paper mills using deinked pulp

Paper and paperboard mills

Building products mills

2. Industrial Practices

The following industrial practices can significantly influence pretreatment:

Pulping Process

The pulping process determines the pulp yield and quality, and the probable organics loss in the wastewater from a pulp mill. (Mechanical pulping results in minimum dissolution of wood components, while chemical pulping solubilizes the non-cellulose components of wood tannins, lignins, wood sugars, and hemicellulose).

Recovery and Reuse of Spent Cooking Liquor

Most chemical pulping processes involve recovery and reuse of spent cooking liquor and therefore do not generate significant quantities of wastewater (1). The dissolved organics present in the liquor usually are burned in the chemical recovery furnace. The only pulping process where the spent cooking liquor is not suitable for recovery is the calcium-base acid sulfite process. The spent cooking liquor from this process, with the dissolved organics, is generally discharged with other process wastes.

Bleaching

When the desired quality of the final product requires bleaching of pulp recovered from wood, it is usually done by the addition of oxidizing chemicals, such as chlorine, chlorine compounds, peroxides, and hydrosulfites. The oxidizing chemicals react with the non-cellulose portion of the pulp, rendering it soluble in water or in alkaline solutions. As a result, the bleaching step adds to the wastewater volume and pollutant loading.

In-Plant Pollution Control Methods

Control of spills and leaks, and recovery and reuse of chemicals constitute the major pollution control practices within the paper and allied products industry. The extent of pretreatment required is largely dependent on the extent and effectiveness of the in-plant control processes adopted.

3. Wastewater Characteristics

The characteristics of the process wastewaters from each pretreatment sub-groups are shown in Table D-1-1.

Integrated pulp and paper mills generally operate continuously throughout the year except for the shutdowns for preventive maintenance and equipment repair and replacement. Modern practice is to employ continuous pulping processes, however some mills are still using batch pulping processes which result in intermittent discharges of wastewater. In addition, some older mills (generally relatively small, less than 100 tons/day) operate only 3 to 5 days per week.

The overall wastewater characteristics from wood pulping processes may vary seasonally because of the changes in characteristics of wood and variations in the temperature of the water. The volume and characteristics of the process wastewater depend upon the degree of water reuse, chemical recovery systems, and the type and quality of paper involved.

The wastewaters generated from the paper and allied products industry contain BOD, COD, suspended solids, dissolved solids, color, acidity or alkalinity, and heat. Chemical pulping processes may produce wastewaters with heavy metals (Cr, Ni, Hg, Pb, Zn). If pulp bleaching is part of the operation, the wastewaters may contain additional heavy metals (Hg) and dissolved solids (chlorides). Mercury may be present in the caustic used in pulping and bleaching operations. Zinc is used in the bleaching of ground wood pulp. Chromium, nickel, and iron may be introduced from the corrosion of process equipment.

When spent cooking liquor recovery is not practiced, the wastewaters may be acidic (pH 2 to 3) and have high concentrations of dissolved organics and inorganics. The solubilized organics and the type of cooking liquor will determine the characteristics of the wastewater.

Major considerations in the joint treatment of paper and allied products industrial wastewaters with domestic wastewaters are the high chlorine demand and nutrient deficiency (phosphorus and nitrogen). These characteristics would significantly influence the kinetics and design of joint treatment facilities. Information available on the joint treatment of paper and allied products wastewaters indicate the following effects:

a. When neutral sulfite semichemical pulping wastewater exceeded approximately 10 percent of the total flow to a publicly owned treatment works, a retardation in the rate of BOD exertion was observed (3). Under such circumstances, the kinetic parameters and oxygen requirements should be established by specific investigation.

b. The activated carbon adsorption process can not be substituted for the biological processes to reduce BOD.

c. Attempts to use the trickling filter process (stone and plastic media) for the treatment of paper mill wastes have achieved only relatively low removals (40-60 percent BOD removal). This has been attributed primarily to high organic loading and filter clogging with fibers (4).

d. Paper mill wastewaters exhibit high chlorine demand values (20-60 mg/L), even after secondary treatment. Depending on the ratio of paper mill wastes to domestic wastes, larger chlorination facilities may be required.

e. When paper mill waste sludge forms a significant portion (approximately 60 percent) of total sludge, longer digestion periods are required for anaerobic digestion (5).

The only exceptions to the wastewater and treatability characteristics noted in the preceding discussion are the wastewater generated from the converted paper and paperboard manufacturing segment of the industry, which segment uses relatively dry processes. Since the process wastewaters from this type of plant are very low in volume and contain as major constituents only BOD and suspended solids, they are readily treatable in municipal systems.

4. Pretreatment

The pretreatment unit operations which may be necessary for various types of joint treatment processes are shown in Table D-1-2.

The neutralization requirements depend primarily on the pulping process and on the related recovery and reuse practices. When spent cooking liquor is discharged to municipal sewers, special care must be taken to insure control of pH, organic shock loads, and color (if present). If bleaching is part of the operation, pH adjustment may be necessary before mixing with other wastes. Spills of spent liquors and pulp washing water may introduce shock loads of pH and organic material if their discharge into the municipal sewer system is not carefully controlled. In the absence of effective in-plant control procedures, adequate equalization and extensive pH and conductivity control may be required to protect the operation of a joint treatment facility.

The heavy metal concentrations in the paper and allied products industry wastewaters are very low and generally do not require pretreatment. Nevertheless, their levels should be determined to insure that effluent limitations are not exceeded where heavy metals are a significant factor.

Table D-1-1

Wastewater Characteristics
Paper and Allied Products

Characteristics	Mechanical Pulping (Bleached & Unbleached)	Chemical Pulping (Unbleached)	Chemical Pulping (Bleached)	Deinking Pulp	Paper and Paperboard	Building Products
Industry Operation	Year-round	Year-round	Year-round	Year-round	Year-round	Year-round
Flow	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous
BOD	EXTREMELY HIGH	AVERAGE-EXT. HIGH	AVERAGE-EXT. HIGH	HIGH	AVERAGE-HIGH	EXTREMELY HIGH
TSS	HIGH	LOW-HIGH	LOW-HIGH	HIGH	AVERAGE-HIGH	EXTREMELY HIGH
TDS	average[1]	HIGH	HIGH	HIGH	Low-average	Low
COD	HIGH	HIGH	HIGH	HIGH	HIGH	HIGH
Grit	PRESENT	PRESENT	PRESENT	PRESENT	PRESENT	PRESENT
Cyanide	Absent	Absent	Absent	Absent	Absent	Absent
Chlorine Demand	HIGH	HIGH	HIGH	HIGH	HIGH	HIGH
pH	neutral[2]	ACID-ALKALINE	ACIDIC	ALKALINE	neutral	Neutral
Color	Low	High	High	Low	Low	Low
Turbidity	High	High	High	High	High	VERY HIGH
Explosives	Absent	Absent	Absent	Absent	Absent	Absent
Dissolved Gases	Absent	Present	Present	Absent	Absent	Absent
Detergents	Absent	Absent	Absent	Absent	Absent	Absent
Foaming	PRESENT	PRESENT	PRESENT	PRESENT	PRESENT	PRESENT
Heavy Metals	ABSENT[3]	PRESENT	PRESENT	PRESENT	Absent	Absent
Colloidal Solids	Present	Present	present	present	present	Present
Volatile Organics	Absent	Present	present	absent	absent	Absent
Pesticides	Absent[4]	Absent[4]	absent[4]	absent	absent	Absent
Phosphorus	DEFICIENT	DEFICIENT	DEFICIENT	DEFICIENT	DEFICIENT	DEFICIENT
Nitrogen	DEFICIENT	DEFICIENT	DEFICIENT	DEFICIENT	DEFICIENT	DEFICIENT
Temperature	HIGH[5]	HIGH[5]	HIGH[5]	HIGH[5]	HIGH[5]	HIGH[5]
Phenol	Absent	Absent	Absent	Absent	Absent	Absent
Sulfides	Absent	Absent	Absent	Absent	Absent	Absent
Oil & Grease	Present	Present	Present	Present	Present	Present
Coliform (Total)	Average	Average	Average	Average	Average	Average

[1] High if bleaching of pulp is practiced.
[2] Acidic if bleaching of pulp is practiced.
[3] Present if bleaching of pulp is practiced.
[4] Present only from log washing operations.
[5] Higher temperature than domestic wastewater. May affect design but not harmful to joint treatment processes.

NOTE: Characteristics which may require pretreatment or are significant to joint treatment plant design are shown in UPPER CASE. The wastewater characteristics shown reflect the Industrial Practices described in Section 2.

Table D-1-2

Pretreatment Unit Operations for the Paper and Allied Products Industry

Pretreatment Sub-Group	Suspended Biological System	Fixed Biological System	Independent Physical - Chemical System
Mechanical Pulping[1] (Unbleached)	Coarse Solids Separation + Grit Removal	Where pulp and paper wastewaters constitute more than about 10 percent of the total wastewater flow, fixed biological systems or independent physical chemical systems normally are not used. Where the pulp and paper wastewater constitute less than this proportion, the pretreatment requirements will be same as for suspended biological systems.	
Mechanical Pulping[1] (Bleached)	Coarse Solids Separation + Grit Removal + Neutralization		
Chemical Pulping[1] (Unbleached)	Coarse Solids Separation + Grit Removal + Neutralization		
Chemical Pulping[1] (Bleached)	Coarse Solids Separation + Grit Removal + Neutralization		
Deinking Pulp[1]	Coarse Solids Separation + Neutralization		
Paper & Paper Board	Coarse Solids Separation		
Building Products	Coarse Solids Separation		

[1] Equalization may be required in addition to those shown when batch pulping processes are used.

REFERENCES

1. "Industrial Waste Survey of the Paper and Allied Products Industries" Contracts #68-01-0022 and 68-01-0012, Environmental Protection Agency, Washington, D.C. (Unpublished)

2. "Paper Mills Industry Wastewater Profile," F.W.P.C.A. Contract #14-12-10, F.W.P.C.A. (November 1967).

3. "Combined Treatment of Sanitary Sewage and Semichemical Pulp Mill Waste," Technical Bulletin #42, National Council for Steam Improvement (1951).

4. "Industrial Wastewater Control," (Edited by) Gurnham, F.C., Academic Press, New York (1965).

5. "Joint Municipal and Semichemical Pulping Waste Treatment," Water Pollution Control Research Series, Publication No. ORD 1 (July 1969).

1. Industry Description

This industry includes Standard Industry Classifications (SIC) 2021, 2022, 2023, 2024, 2026, and 5043. These classifications include bulk handling, packaging, and processing (pasteurizing, homogenizing, and vitaminizing) of milk, and the manufacture of dairy products including butter, cheese, ice cream, condensed evaporated milk, and dry milk and whey.

The manufacture of dairy products involves receiving and storing raw milk, separation of excess cream, pasteurization and homogenization, fluid milk packaging, and making butter, ice cream, and cheese. In the separation step, excess cream may be skimmed off in order to standardize the butter fat content, or the raw milk may be separated by centrifuge into cream and skim milk. Separated cream is then used in butter or ice cream making, while the skim milk may be used in the production of cottage cheese and non-fat dry milk solids. Natural cheese (i.e., not cottage cheese) is made with whole milk.

Some of these processes generate by-products which may be recovered and utilized in other food manufacturing operations. Buttermilk, skim milk, and whey are produced from butter and cheese making. The regional market potential for these by-products often determines the amount of in-plant recovery.

The dairy industry is a year-round operation. Raw-milk receiving stations handle milk from the local farms for subsequent transfer to tank trucks. These stations are operated on an intermittent daily basis. The rest of the industry will operate either continuously or on an intermittent basis depending on the economics of the individual facility. In general, larger processing plants tend to be integrated plants producing more than one product.

The pretreatment sub-groups for this industry are as follows:

Cottage and Natural Cheese Products
Milk Handling and Products.

2. Industrial Practices

Product recovery is the major method for reducing wastewater loadings. The dairy industry, however, must maintain sanitary conditions and this tends to limit the amount of wastewater recycle which is practicable.

The following industrial practices can have a major impact on the wastewater characteristics:

Whey Handling

Whey can be condensed and dried, and used as a food and feed supplement. However, there are inherent difficulties in drying the acid whey derived from cottage cheese because of its lactic acid content.

Operating Procedures

Spillage, overflow, and leakage caused by improperly maintained equipment and poor operating procedures can result in major pollutional loads due to the concentrated nature of the dairy products, e.g., whole milk has a BOD over 100,000 mg/L (0.8 pounds of BOD for every gallon of milk lost) (1).

Cleaning

High efficiency in sanitizing operations is important to minimize the usage of sanitizers and detergents. In addition, rinses can be collected and used as make-up water for sanitizers (2). Milk processing lines should be sloped to central collection points so that the milk product may be collected before the lines are sanitized.

3. Wastewater Characteristics

The characteristics of the process wastewaters from each pretreatment sub-group are shown in Table D-2-1.

Daily wastewater flows are characterized as intermittent because some major unit processes, e.g., cheese and butter making, are batch, and because milk processing equipment must be shut down daily for sanitizing to maintain rigid health standards. Relatively clean water may be a substantial portion of the total wastewater from a dairy plant. These waters are from condensers, refrigeration compressors, milk coolers, and air conditioning systems.

The major types of wastewaters from the dairy industry are:

1. Wash and rinse water from cans, tank trucks, equipment, and floors. In general, the pH of the wastewater will be affected by the cleaning compound

(either acid or alkali) and the proportion of the wash water in the total plant wastewater flow.

2. By-products (such as buttermilk, skim milk, or whey) they are sewered rather than recovered. Buttermilk and skim milk have BOD values as high as 70,000 mg/L, while the BOD of whey is 50,000 mg/L (3).

3. Entrainment from evaporators and the sewering of spoiled or damaged products.

The wastewaters generated in the dairy industry can be characterized generally as containing high concentrations of BOD, COD, and TDS. Settleable solids are not an important consideration in most dairy wastewaters, since all the organic material is in a colloidal or dissolved state. However, sand or other gritty material may be present from tank truck washings (4). Cheese wastewaters, on the other hand, have higher concentrations of settleable solids due to the presence of curd solids.

Design considerations in the joint treatment of dairy and domestic wastewaters are the high chlorine demand and the presence of surface-active agents, coliforms, and high-septicity potential. In addition, cheese production wastewaters are usually nitrogen-deficient. Septicity should be a consideration in the design of any equalization or clarification facilities. Wastewater temperature normally would not be a consideration because of dilution in the municipal collection system.

Low-rate trickling filters are generally not effective in treating dairy wastes, because these wastes produce large quantities of biological solids which clog the filters. This problem can be overcome by high hydraulic loading and high recirculation rates (3).

4. Pretreatment

The pretreatment unit operations which may be necessary for various types of joint treatment facilities are shown in Table D-2-2.

In general, dairy wastes are amenable to biological as well as to chemical treatment if equalization and neutralization are provided as pretreatment for the dairy wastes. As the ratio of dairy waste to domestic waste increases, the need for the suggested pretreatment also increases markedly. Where whey is present, it may be necessary to control the rate of discharge and to provide nutrient supplements at the joint treatment plant.

Table D-2-1

Wastewater Characteristics
Dairy Products

Characteristics	Milk Handling Milk Products	Natural and Cottage Cheese Product
Industrial Operation	Year-round (BATCH)	Year-round (BATCH)
FLOW	INTERMITTENT	INTERMITTENT
BOD	Average-HIGH	EXTREMELY HIGH
TSS	Low-Average	Average-EXT. HIGH
TDS	Average-HIGH	HIGH
COD	Average-HIGH	EXTREMELY HIGH
Grit	PRESENT	PRESENT
Cyanide	Absent	Absent
Chlorine Demand	HIGH	HIGH
pH	ACID TO ALKALINE	ACID TO ALKALINE
Color	HIGH	HIGH
Turbidity	High	High
Explosives	Absent	Absent
Dissolved Gases	Absent	Absent
Detergents[1]	PRESENT	PRESENT
Foaming	PRESENT	PRESENT
Heavy Metals	Absent	Absent
Colloidal Solids	HIGH	HIGH
Volatile Organics	Absent	Absent
Pesticides	Absent	Absent
Phosphorus	Present	Present
Nitrogen	Adequate	DEFICIENT
Temperature	Normal-High[2]	Normal-High[2]
Phenol	Absent	Absent
Sulfides	Absent	Absent
Oil and Grease	Present	Present
Coliform	PRESENT	PRESENT

[1] There are possible bio-static effects in the joint treatment plant attributable to large amounts of sanitizers and detergents in the dairy products wastewater.

[2] Temperature equal to or higher than domestic wastewater. May affect design but not harmful to joint treatment processes.

NOTES: Characteristics which may require pretreatment or are significant to joint treatment plant design are shown in UPPER CASE.

Wastewater characteristics shown reflect all the Industrial Practices described under Section D-2.

Table D-2-2

Pretreatment Unit Operations for the Dairy Products Industry

Pretreatment Sub-Group	Suspended Biological System	Fixed Biological System	Independent Physical Chemical System
Milk Handling Milk Products	Equalization + Neutralization	Equalization + Neutralization	Equalization + Neutralization
Natural and Cottage Cheese Products	Equalization + Neutralization	Equalization + Neutralization	Equalization + Neutralization

REFERENCES

1. "Proceedings Second National Symposium on Food Processing Wastes", Denver, Colorado, Environmental Protection Agency, Water Pollution Control Research Series 12060 (March, 1971).

2. "The Cost of Clean Water, Vol. III. Industrial Profile No. 9 - Dairies". Federal Water Pollution Control Administration, Washington, D.C. (June, 1967).

3. "Study of Wastes and Effluent Requirements of the Dairy Industry", Contract No. 68-01-0023, Environmental Protection Agency, Washington, D.C. (Unpublished).

4. "Industrial Wastewater Control". (Edited by) Gurnham, C.F., Academic Press, New York (1965).

1. Industry Description

This industry includes Standard Industry Classifications (SIC) 2231, 2250, 2260, 2270, 2284, and 2297.

The textile industry involves the manufacture of fabrics from wool, cotton, and synthetic fibers; the synthesis or spinning of synthetic fibers is not included in this group, but rather is included under synthetic organic chemicals. Of the three major textiles, wool represents the smallest market and synthetic textiles the largest.

The major unit processes of the woolen textile industry include scouring, dyeing, fulling, carbonizing, bleaching, and weaving.

Raw wool is scoured to remove grease and dirt. The process employs a detergent and mild alkali at temperatures of 130°F. This operation is responsible for 55-75 percent of the total BOD load from wool finishing (1).

The dyeing process uses dyes, dyeing assistants, (e.g. acetic acid, ammonium sulfate), and dye carriers containing heavy metals. The dye carriers will be present only if the wool is being combined with a synthetic fabric, which requires a dye carrier to facilitate dye penetration (2).

Various chemicals (e.g. sulfuric acid, hydrogen peroxide, and olive oil) may be added before and during the fulling operation. These chemicals then enter the wastewater during a subsequent washing step.

Carbonizing impregnates the wool with sulfuric acid to remove any traces of vegetable matter. Bleaching may then be accomplished, with either sulfur dioxide, hydrogen peroxide, or optical brighteners.

The major unit processes employed in the cotton and synthetic textile industry include sizing, weaving, desizing, scouring, dyeing, and finishing. Chemicals used in the sizing process include starch, polyvinyl alcohol, carboxymethyl cellulose, and polyacrylic acid.

After weaving, the fabric is desized using an acid enzyme reaction. Desizing removes the chemicals added during sizing by hydrolyzing them to a soluble form.

During scouring cotton wax and other non-cellulosic components of cotton are removed by using hot alkaline solutions. Synthetic materials require only light scouring because of the absence of chemical impurities (3).

Both cotton and synthetic fabrics are treated with special finishes, using formaldehyde and urea, and with fire retardants, such as triaziridyl phosphine oxide.

The pretreatment sub-groups for this industry are:

Wool
Cotton and Synthetic Fabrics

2. Industrial Practices

The following industrial practices can significantly affect the wastewater characteristics:

Segregation of Waste Streams

The segregation of waste streams permits recovery of heavy metals, caustic recovery and reuse, and control of toxic spills (such as dieldrin used for mothproofing). Many of the older textile mills have a common collection system with chemical reuse, but the modern mills have a segregated collection system to permit chemical recovery and reuse.

Alkaline Wool Scouring

Alkaline wool scouring may be used in place of neutral scouring. In alkaline scouring, soda ash is added to the wash water and subsequently combines with a portion of the wool grease to from natural soap. This procedure reduces the amount of detergent required and reduces the BOD and the concentration of residual surface-active agents.

Chemical Sizing

The substitution of polyvinyl alcohol or carboxy methylcellulose for starch in the sizing of cotton reduces the overall BOD in the wastewater.

Pressure Dyeing Becks

The use of pressure dyeing becks in the place of atmospheric units permits reduction in the amount of dye carriers required thereby reducing the BOD and heavy metal concentrations.

3. Wastewater Characteristics

The characteristics of the process wastewaters from each pretreatment sub-group are shown in Table D-3-1.

The textile industry generally operates continuously throughout the year except for scheduled shutdowns. However, many of the individual unit operations within the industry are batch oriented. Daily wastewater flows are continuous with peak flows occurring if certain batch-type operations are used. The textile industry is usually in a state of flux, with the manufacturing process continually being modified to reflect changes in consumer trends.

Wastewaters generated in the textile industry are high in BOD, COD, TDS, and color. For synthetics, dyeing results in the largest BOD contribution, attributed to the use of dye carriers such as methyl naphthalene, biphenyl, and orthophenyl phenol, all of which have a high BOD. For cotton finishing, desizing contributes about 45 percent of the total BOD, scouring about 30 percent, and dyeing about 17 percent (1). The most significant difference between wool process wastewaters and those from the rest of the industry is the release of wastewaters with high concentrations of suspended solids and grease from the wool-scouring operation.

Textile wastewaters can vary from slightly acid to highly alkaline depending on the individual processes carried out within the plant. They generally are alkaline when caustic scouring or mercerizing is involved. Heavy metals such as copper, chromium and zinc result from the use of certain dye carriers in the dyeing operation of synthetic fabrics and of blended fabrics, e.g. cotton and rayon.

4. Pretreatment

The pretreatment unit operations which may be necessary for various types of joint treatment facilities are shown in Table D-3-2.

Table D-3-1

Wastewater Characteristics
Textile Industry

Characteristics	Wool	Cotton and Synthetics
Industrial Operation	Year-round (batch)	Year-round (batch)
Flow	INTERMITTENT[1] - Continuous	INTERMITTENT[1] - Continuous
BOD	HIGH	Average-HIGH
TSS	HIGH	Low-AVERAGE
TDS	HIGH	HIGH
COD	HIGH	Average-HIGH
Grit	PRESENT	Absent
Cyanide	Absent	Absent
Chlorine Demand	HIGH	HIGH
pH	BASIC	BASIC
Color	HIGH	HIGH
Turbidity	High	High
Explosives	Absent	Absent
Dissolved Gases	Absent	Absent
Detergents	PRESENT	PRESENT
Foaming	Present	Present
Heavy Metals	PRESENT	PRESENT
Colloidal Solids	Present	Present
Volatile Organics	Absent	Absent
Pesticides	Absent	Absent
Phosphorus	PRESENT	PRESENT
Nitrogen	DEFICIENT	DEFICIENT
Temperature	Normal-High[2]	Normal-High[2]
Phenol	Absent[3]	Absent[3]
Sulfides	Absent	Absent
Oil and Grease	HIGH[5]	Absent-Present[4]
Coliform (Fecal)	PRESENT	Absent

[1] Wastewater flow characterized by an intermittent pattern over the day.

[2] Temperature equal to or higher than domestic wastewater. May affect design but not harmful to joint treatment processes.

[3] Phenol may be present in dye carriers.

[4] Oil present in wastewaters from synthetic textiles only.

[5] Wool processing wastewaters contain high concentration of animal grease.

NOTES: Characteristics which may require pretreatment or are significant to joint treatment plant design are shown in UPPER CASE.
Wastewater characteristics shown do not reflect the industrial practices described in Section 2.

Table D-3-2

Pretreatment Unit Operations for the Textile Industry

Pretreatment Sub-Group	Suspended Biological System	Fixed Biological System	Independent Physical - Chemical System
Wool	Coarse Solids Separation + Grease Removal + Chemical Precipitation (color, heavy metals) + Equalization + Neutralization	Coarse Solids Separation + Grease Removal + Chemical Precipitation (color, heavy metals) + Equalization + Neutralization	Coarse Solids Separation + Grease Removal + Chemical Precipitation (color, heavy metals) + Equalization + Neutralization
Cotton & Synthetics	Coarse Solids Separation + Chemical Precipitation (color,heavy metals) + Equalization + Neutralization	Coarse Solids Separation + Chemical Precipitation (color,heavy metals) + Equalization + Neutralization	Coarse Solids Separation + Chemical Precipitation (color,heavy metals) + Equalization + Neutralization

REFERENCES

1. "State of the Art of Textile Waste Treatment". Water Pollution Control Research Series, 12090 ECS; Environmental Protection Agency, Washington, D.C. (1971).

2. "Industrial Waste Studies Program - Textile Mill Products", Environmental Protection Agency (Unpublished)

3. "The Cost of Clean Water - Vol. III - Industrial Waste Profile No. 4 Textile Mill Products", Federal Water Pollution Control Administration (September, 1967).

1. Industry Description

This Industry includes Standard Industry Classifications (SIC) 2031, 2036, and 2094

The seafood industry is made up of many processing centers, located along the United States coastlines, with a number of the larger plants remotely located with respect to neighboring industry and population centers. The annual U.S. catch in 1968 was approximately 4 billion pounds (cleaned) with the catch being utilized as follows: 35% rendered, 30% marketed fresh, 20% canned, 10% frozen, and 5% to miscellaneous processing (1).

The seafood industry involves the processing of numerous species of seafood including: mollusks (oysters, clams, and scallops); crustaceans (crabs and lobsters); and various species of both salt- and fresh-water fish.

This industry uses the following major unit processes (1, 2): washing, eviscerating, dressing, processing, and rendering. Solid waste from these processes is significant. Average wastage for all fish and shellfish is about 30% of body weight, with values ranging from zero for whole rendered fish to 85% for some crabs (1). Some boats eviscerate and clean fish at sea, thereby decreasing waste quantities at the shore-side processing plant. Many plants use substantial amounts of sea water for cleaning operations.

Rendering of whole fish and fish by-products produces fish meal, oil, and solubles. Currently, four classes of rendering processes are used: dry, wet, solvent extraction, and digestion. Wet rendering is the most prominent process. In this process, the by-products are cooked with steam, and the material is pressed to yield a solid cake and press liquor. The liquor is centrifuged to obtain fish oil and stick water. The stick water is evaporated to give condensed fish solubles.

Because of the similarity of the pollutants significant to pretreatment of wastewaters from the seafood industry, there are no separate pretreatment sub-groups for this industry.

2. Industrial Practices

The following industrial practices can significantly influence the wastewater characteristics.

Solid Waste Handling

The handling of the solid process wastes in a dry form substantially decreases waste loadings in the wastewater.

Process Water Conservation

New techniques may be introduced to reduce the amount of process water usage, e.g., using counter-current washing.

3. Wastewater Characteristics

The characteristics of the process wastewaters from the industry are shown in Table D-4-1.

The seafood processing industry is seasonal, but wastewater flows are relatively constant during operation. Wastewaters include various auxiliary sources such as cooling water and cooling waters from refrigeration systems.

The wastewaters generated from seafood processing contain as major constituents BOD, COD, TSS, TDS, and oil. The occurrence of the oil component depends on whether oily or non-oily seafood is being processed and the processing operations employed. Considerations of significance to the joint treatment of seafood wastewaters and domestic waste include high chlorine demand, the presence of surface-active agent, fecal coliform, and high concentrations of chlorides and other dissolved solids from sea water usage within the plant.

4. Pretreatment

The pretreatment unit operations which may be necessary for various types of joint treatment facilities are shown in Table D-4-2.

Very little treatability information is available for seafood-processing wastewaters. If seawater is used as process water, a sufficient dilution of the process water by domestic wastewater is required so that dissolved solids and chlorides will not cause problems in a joint biological treatment plant. When seawater is used exclusively, the dilution ratio should be about 3 parts domestic wastewater to 1 part seawater. Oil separation may be a pretreatment consideration if oily fish, such as tuna, sardines, herring, cod, haddock, halibut, etc., are processed in a manner which results in significant quantities of oil in the wastewater.

Table D-4-1

Wastewater Characteristics
Seafood Industry

Characteristics	Classification
Industrial Operation	SEASONAL
Flow	Continuous
BOD	Average-HIGH
TSS	Average-HIGH
TDS	Average-HIGH
COD	Average-HIGH
Grit	Absent
Cyanide	Absent
Chlorine Demand	Average-HIGH
pH	Neutral
Color	Average-HIGH
Turbidity	High
Explosives	Absent
Dissolved Gases	Absent
Detergents	Present
Foaming	Absent
Heavy Metals	Absent
Colloidal Solids	Average-HIGH
Volatile Organics	Absent
Pesticides	Absent
Phosphorus	Adequate
Nitrogen	Adequate
Temperature	Normal-High[1]
Phenol	Absent
Sulfides	Absent
Oil & Grease	Average-HIGH[2]
Coliform (Fecal)	PRESENT
Coliform (Total)	PRESENT

---

[1] Temperature equal to or higher than domestic wastewater. May affect design but not harmful to joint treatment processes.

[2] Depending upon whether oily or non-oily seafood is being processed.

NOTE: Characteristics which may require pretreatment or are significant to joint treatment plant design are shown in UPPER CASE.
Wastewater characteristics shown reflect the handling and disposal of solid wastes in dry form as described in Section 2.

Table D-4-2

Pretreatment Unit Operations for the Seafood Industry

Suspended Biological System	Fixed Biological System	Independent Physical Chemical System
Coarse Solids Separation + grit removal[1] + oil separation[2]	Coarse Solids Separation + grit removal[1] + oil separation[2]	Coarse Solids Separation + grit removal[1] + oil separation[2]

---

[1] For shellfish processing.

[2] Oil separation may be required to reduce free floating oil and grease depending on seafood processed.

REFERENCES

1. "Current Practice in Seafoods Processing Waste Treatment", Water Pollution Control Research Series, 12060 ECF, Environmental Protection Agency, Washington, D.C. (April, 1970).

2. "Industrial Wastewater Control". (Edited by) Gurnham, C.F., Academic Press, New York (1965).

1. Industry Description

This industry includes Standard Industry Classifications (SIC) 2831, 2833, and 2834. The industry produces medicinal chemicals and pharmaceutical products, including some fine chemicals which are marketed outside the pharmaceutical industry as intermediates.

In 1970, there were 1,300 producers of pharmaceuticals in the United States, and 150 of these firms produced over 95% of the industry's products (1).

In general, the pharmaceutical industry may be divided into two broad production categories; chemical synthesis products; and antibiotics (penicillin and steroids).

The manufacturing operations for synthesis products may be either dry or wet. Dry production involves dry mixing, tableting or capsuling, and packaging. Process equipment is generally vacuum cleaned to remove dry solids and then washed down.

The production of wet synthesis products and antibiotics is very similar to fine chemicals production, and uses the following major unit processes: reaction, extraction and concentration, separation, solvent recovery, and drying.

Wet synthesis reactions generally are batch types followed by extraction of the product. Extraction of the pharmaceutical product is often accomplished through solvents. The product may then be washed, concentrated and filtered to the desired purity, dried, capsulized, and packaged.

The production of antibiotics is restricted to a few of the larger pharmaceutical firms. Some antibiotics are produced in batch fermentation tanks in the presence of a particular fungus or bacterium. The culture frequently is filtered from the medium and marketed in cake or liquid form as an animal feed supplement (2). The antibiotic is extracted from the culture medium through the use of solvents, activated carbon, etc. The antibiotic is then washed to remove residual impurities, concentrated, filtered, and packaged.

The pretreatment sub-groups for this industry are as follows:

Synthesis
Fermentation

2. Industrial Practices

The following industrial practices can significantly influence the wastewater characteristics:

1. Solvent recovery is practiced in both the synthesis and the fermentation products segment of the industry. Certain products may require a high-purity solvent in order to achieve the required extraction efficiency required (3). This increases the incentive for making the recovery process highly efficient.

2. Some solvent streams which cannot be recovered economically, are incinerated. Incineration is also used to dispose of "still bottoms" from solvent recovery units.

3. Wastewater Characteristics

The characteristics of the process wastewaters from each pretreatment sub-group are shown in Table D-5-1.

The pharmaceutical plants operate continuously throughout the year and are characterized by batch operations with significant variations in pollutional characteristics over any typical operating period.

The major sources of wastewaters are product washings, concentration and drying procedures, and equipment washdown. Wastewaters generated from the pharmaceutical industry can be characterized as containing high concentrations of BOD, COD, TSS, and volatile organics. Wastewaters from some wet chemical syntheses may contain heavy metals (Fe, Cu, Ni, V, Ag) or cyanide, and generally have anti-bacterial constituents, which may exert a toxic effect on biological waste treatment processes.

Considerations significant to the design of joint treatment works are the highly variable BOD loadings, high chlorine demand, presence of surface-active agents, and the possibility of nutrient deficiency.

4. Pretreatment

The pretreatment unit operations which may be necessary for various types of joint treatment facilities are shown in Table D-5-2.

The specific type and degree of pretreatment for heavy metals and cyanide will be governed by the industrial effluent guidelines for the pharmaceutical industry. Cyanide removal or control is especially important.

Pharmaceutical industries generate wastewaters on an intermittent basis and equalization may be needed as pretreatment. When solvents are used for extraction, solvent removal can be accomplished by using gravity separation and skimming. Neutralization may be required to neutralize acidic or alkaline wastewaters generated from the production of specific pharmaceutical products.

Table D-5-1

Wastewater Characteristics
Pharmaceutical Industry

Characteristics	Synthesis	Fermentation
Industrial Operation	Year-Round (BATCH)	Year-Round (BATCH)
Flow	INTERMITTENT	INTERMITTENT
BOD	AVERAGE-HIGH	EXTREMELY HIGH
TSS	HIGH	EXTREMELY HIGH
TDS	AVERAGE-HIGH	HIGH
COD	AVERAGE-HIGH	EXTREMELY HIGH
Grit	Absent	Absent
Cyanide	PRESENT	Absent
Chlorine Demand	AVERAGE-HIGH	HIGH
pH	ACID-BASIC	ACID-BASIC
Color	Average-High	Average-High
Turbidity	Average	High
Explosives	Present	Present
Dissolved Gases	Absent	Absent
Detergents	PRESENT	PRESENT
Foaming	PRESENT	PRESENT
Heavy Metals	PRESENT	Absent
Colloidal Solids	High	HIGH
Volatile Organics	HIGH	HIGH
Pesticides	Absent	Absent
Phosophorus	DEFICIENT	DEFICIENT-HIGH
Nitrogen	DEFICIENT	DEFICIENT-HIGH
Temperature	Normal-High[1]	Normal-High
Phenol	Absent	Absent
Sulfides	Absent	Absent
Oil & Grease	Absent-Present	Absent-Present
Coliform (Total)	Absent	Absent-Present

[1] Temperature equal to or higher than domestic wastewater. May affect design but not harmful to joint treatment processes.

NOTES: Characteristics which may require pretreatment or are significant to joint treatment plant design are shown in UPPER CASE.
Wastewater characteristics shown reflect all the Industrial Practices described in Section 2.

Table D-5-2

Pretreatment Unit Operations for the Pharmaceutical Industry

Pretreatment Sub-Group	Suspended Biological System	Fixed Biological System	Independent Physical Chemical System
Synthesis	Chemical Precipitation (Heavy Metals) + Solvent Separation + Neutralization + Cyanide Oxidation	Chemical Precipitation (Heavy Metals) + Solvent Separation + Equalization + Neutralization + Cyanide Oxidation	Chemical Precipitation (Heavy Metals) + Solvent Separation + Equalization + Neutralization + Cyanide Oxidation
Fermentation	Solvent Separation + Equalization + Neutralization	Solvent Separation + Equalization + Neutralization	Solvent Separation + Equalization + Neutralization

REFERENCES

1. Lund, H.F., "Industrial Pollution Control Handbook", McGraw-Hill Book Co., New York (1971).

2. "Industrial Wastewater Control", (Edited by) Gurnham, C.F., Academic Press, New York (1965).

3. Rudolfs, W., "Industrial Wastes, Their Disposal and Treatment", Reinhold Publishing Corp., New York (1953).

LEATHER TANNING AND FINISHING INDUSTRY

1. Industry Description

This industry includes Standard Industrial Classification (SIC) 3111. This classification includes tanning, curing, and finishing hides and skins into leather. The trend in the tannery industry is toward greater centralization near large metropolitan areas. This results in an increased number of municipal treatment plants treating tannery wastes. Approximately 80 percent of the output from tanneries is from cattle-hide processing, with the remainder being pigskin, calfskin, goatskin, and sheepskin processing (1).

The tanning process involves conversion of animal hide and skins into leather. The grain layer and the corium portion of the skins constitute the leather-making material and consist mainly of the protein collagen. During the tanning process, the collagen fibers are reacted with tannin, chromium, alum, or other tanning agents to form the leather. Four basic operations are involved in tanneries:

1. Beam House
2. Tan House
3. Retan, color and fat liquor
4. Finishing

The beam house operation involves: storage and trimming of hides; washing and soaking to remove dirt, salt, blood, manure and non-fibrous proteins; green fleshing for the removal of adipose fatty tissues and meat; unhairing to remove epidermis and hair; bating to remove non-collagenous proteins; and pickling in some current operations to stabilize and preserve the unhaired stock for subsequent operations. The beam house operation is typical of hide and skin processing with cattlehide processing being the most important in the U.S.

The tan house operation consists of preparing the stock for tanning. Pickling is done to make the skin acid enough to prevent precipitation of chromium during tanning. Two types of tanning are common in the United States: vegetable tanning; and chrome tanning. Vegetable tanning, the older process, is carried out in a solution containing plant extracts (such as vegetable tannin) to produce heavy leathers such as sole leathers and saddle leathers. Light leathers, such as shoe upper leathers, are usually chrome-tanned by immersion in a bath containing proprietary mixtures of basic chromium sulfate.

Hides which have not been fully tanned in the chrome-tanning process may be retanned with either chrome, vegetable, or synthetic tanning agents. The fat liquor process involves the addition of many types of oils and greases to the tanned hides to prevent cracking and to make the leather soft, pliable, strong, and resistant to tearing. Coloring or dyeing of tanned leather may be done either before or after fat liquoring and uses either natural or synthetic dyestuffs. Finishing operations such as drying, coating, staking, and plating follow the foregoing wet processes.

The pretreatment sub-groups for this industry are:

Chrome Tanning
Vegetable Tanning

2. Industrial Practices

In-plant pollution control techniques and chemical recovery practices in tanneries vary depending on the tanning process and the economics of chemical recovery systems. In vegetable tanning, it is common practice to recycle the tanning solution. (In chrome tanning, a number of tanneries are practicing recycling of tanning solution.) Recovery of grease is normally practiced in pigskin and sheepskin tanneries.

The wastewater characteristics from the unhairing process will depend on whether the industry is practicing a "save hair" or "pulp hair" operation. A low amount of sulfide (0.5 to 1.0 percent of hide weight) removes the hair with minimal damage, while a high amount (2 to 3 percent) pulps and partially dissolves the hair. The "save hair" operation involves mechanical pulling and recovery of hair. Dissolution of hair through chemical reactions is referred to as "pulping" or "burning".

3. Wastewater Characteristics

The characteristics of the process wastewaters from each pretreatment sub-group are shown in Table D-6-1.

Most sub-processes within the tanneries are batch operated, and, therefore, the wastewater flow and characteristics fluctuate during the industry operation. In addition, week-end shutdowns in some tanneries will result in wastewater flow only during weekdays. The seasonal variations in wastewater flow are limited to the variations in hide characteristics. In general, the waste characteristics and volume vary widely throughout the day and throughout the week in tanneries. The concentrated waste fractions (lime liquors and spent tan solutions) are derived from batch-type processes. These fractions are therefore discharged intermittently (2, 3, 4, 5).

Liquid process wastes are generated in tanneries from soaking and washing, fleshing, unhairing, bating, pickling, tanning, coloring, and fat liquoring. Auxiliary wastewaters from tanneries result primarily from boiler blowdown and from cooling, and represent only a minor fraction of the total waste load from tanneries. Therefore, only process waste streams are considered for establishing wastewater characteristics and recommending pretreatment.

The characteristics of wastewaters from tanneries vary according to the type of hide processed and the tanning process (vegetable or chrome tanning) used. The tanning process is more of an art than science, and as a result the wastewater characteristics can vary widely for the same type of hide and tanning process. The process wastewaters from tanneries contain as major constituents: BOD, COD, chromium, oil and grease, sulfide, suspended and dissolved solids, alkalinity, hardness, color, and sodium chloride. Significant pollutants that may be present in tannery wastes include: hair, hide, scraps, bits of flesh, blood, manure, dirt, salts, suspended lime, soluble proteins, sulfites, sulfides, amines, chromium salts, vegetable tannin, soda ash, sugar and starches, oils, fats and grease, surface active agents, mineral acids, and dyes (6) which contribute to the BOD and COD.

In general, washing, fleshing, and unhairing operations produce 50 percent of the total volume and approximately 70 percent of the pollutional load from tanneries. The tanning process generates from 5 to 20 percent of wastewater volume and loading (1). The dry finishing operations produce only minor quantities of wastewater from clean-up operations.

The major wastewater sources from tanneries are the beam house and the tan house operations. The beam house wastewater is highly alkaline due to the large quantities of lime used in the process. The wastewater generated from the tan house is generally acidic due to the discharge of spent tanning solution. Normally, these wastewaters are discharged to a common collecting sewer before treatment or discharge to a municipal system. The unregulated batch dumping from bean house and tan house result in a total waste stream with varying pH values.

Mixing alkaline waste streams (from the beam house) with the acidic chrome tanning wastes would result in partial precipitation of chromium, which can be removed by clarification. There is also the hazard of the evolution of H_2S gas. Average chromium concentrations in the total tannery waste can be as high as 300 mg/L in the chrome tanning process.

The other major pollutant in tannery waste is the effluent from the lime-sulfide unhairing operation. The concentration of sulfides in tannery wastes may vary between 30 and 100 mg/L in the total effluent (2). The consequences of release of H_2S gas in the sewer lines and the effect of reducing characteristics of the sulfides on biological treatment processes should be taken into consideration in the design of joint treatment works. Hydrogen sulfide is readily released from solution as a corrosive and extremely toxic gas with an obnoxious odor. By controlling the pH of the solution above 10.0, the H_2S release can be minimized. If the pH of the wastewater is expected to be lower, the sulfide concentration should be reduced below 1.0 mg/L to prevent H_2S odor problems.

In general, tannery wastewaters are amenable to joint treatment by conventional methods, if the industrial wastewater is adequately pretreated. Most available information on the combined treatment of tannery and municipal wastewaters is from bench-scale or pilot plant operations, rather than from full-scale plant operation. This information indicates that when the tannery waste does not exceed about 10 percent of the total flow and when the tannery discharge is regular and well equalized, no difficulty with conventional sewage treatment is likely to occur (7). The tannery waste solids from the vegetable tanning process can amount to approximately 30 percent before seriously impairing gas production in anaerobic digestion. However, digestion of solids developed from chrome tannery wastes may result in gradual build-up of chromium in the digester and eventual failure of the process.

4. Pretreatment

The pretreatment unit operations which may be necessary for various types of joint treatment processes are shown in Table D-6-2. Screening to remove debris, equalization to provide uniformity of effluent, and neutralization with precautions for possible generation of hydrogen sulfide gas, to prevent excessively high pH values are generally necessary prior to discharge to a municipal collection system. Chemical precipitation may be needed to reduce the amount of chromium in the effluent.

The considerations in Table D-6-2 are based on the assumption of fat and grease recovery as a by-product. Where this is not practiced, grease removal facilities may also be needed.

Table D-6-1

Wastewater Characteristics
Leather Tanning and Finishing Industry

Characteristics	Chrome Tanning	Vegetable Tanning
Industry Operation	Year-Round (Batch)	Year-Round (Batch)
Flow	INTERMITTENT	INTERMITTENT
BOD	EXTREMELY HIGH	EXTREMELY HIGH
TSS	EXTREMELY HIGH	EXTREMELY HIGH
TDS	HIGH	HIGH
COD	EXTREMELY HIGH	EXTREMELY HIGH
Grit	PRESENT	PRESENT
Cyanide	Absent	Absent
Chlorine Demand	High	High
pH	ACID - ALKALINE	ACID - ALKALINE
Color	Present	Present
Turbidity	Present	Present
Explosives	Absent	Absent
Dissolved Gases	Present	Present
Detergents	Present	Present
Foaming	Absent	Absent
Heavy Metals	PRESENT	Absent
Colloidal Solids	Present	Present
Volatile Organics	Present	Present
Pesticides	Absent	Absent
Phosphorus	DEFICIENT	DEFICIENT
Nitrogen	Adequate	Adequate
Temperature	Normal[1]	Normal[1]
Phenol	Absent	Absent
Sulfides	Present	Present
Oil & Grease	HIGH[2]	HIGH[2]
Coliform (Total)	Low	Low

---

[1] Temperature equal to domestic wastewater.

[2] Oil and grease (animal origin) are significant only in pigskin and sheepskin processing wastewaters.

NOTES: Characteristics which may require pretreatment or are significant to joint treatment plant design are shown in UPPER CASE.
Wastewater characteristics shown reflect all the Industrial Practices described in Section 2.

Table D-6-2

Pretreatment Unit Operations for the Leather Tanning and Finishing Industry

Pretreatment Group	Suspended Biological System	Fixed Biological System	Independent Physical Chemical System
Chrome Tanning	Coarse Solids Separation + Grit Removal + Equalization + Chemical Precipitation (Heavy Metals) + Solids Separation + Neutralization	Coarse Solids Separation + Grit Removal + Equalization + Chemical Precipitation (Heavy Metals) + Solids Separation + Neutralization	Coarse Solids Separation + Grit Removal + Equalization
Vegetable Tanning	Coarse Solids Separation + Grit Removal + Equalization + Neutralization	Coarse Solids Separararation + Grit Removal + Equalization + Neutralization	Coarse Solids Separation + Grit Removal + Equalization

---

1. Pretreatment requirements assume fat and grease recovery as saleable by-product.

REFERENCES

1. "The Cost of Clean Water, Vol. III, Industrial Waste Profiles No. 7 - Leather Tanning and Fisnishing," U.S. Department of the Interior, FWPCA (1967).

2. "Activated Sludge Treatment of Chrome Tannery Wastes," Water Pollution Control Research Series, ORD-5, U.S. Department of the Interior, FWPCA, (1969).

3. Eye, D. J., Adldons, J. G., "Anaerobic - Aerobic Treatment of Spent Vegetable Tan Liquors from a Sole Leather Tannery," Proc. 23rd Industrial Waste Conference, Purdue University, 126-139 (1968).

4. Sproul, O. J., Keshavan, K., and Hunter, R. W., "Extreme Removals of Suspended Solids and BOD in Tannery Wastes by Coagulation with Chrome Tan Dump Liquors," Proc. 21st Industrial Waste Conference, Purdue University, 600-612 (1966).

5. Nemerow, N. L., and Armstrong, A., "Combined Tannery and Municipal Waste Treatment," Proc. 21st Industrial Waste Conference, Purdue University, 447-467 (1966).

6. "Effluent Requirements for the Leather Tanning and Finishing Industry," by Stanley Consultants, Inc., Muscatine, Iowa, for the Water Quality Office, Environmental Protection Agency, Contract No. 68-01-0024 (Unpublished).

7. Wims, F. J., "Treatment of Chrome Tanning Wastes for Acceptance by an Activated Sludge Process," Proc. 18th Industrial Waste Conference, Purdue University, 534-549 (1963).

1. Industry Description

This industry includes Standard Industrial Classifications (SIC) 2061, 2062, and 2063. These classifications include establishments engaged in the manufacture of raw sugar, syrup, or finished (granulated or clarified) sugar from sugar cane, and the manufacture of sugar from sugar beets.

Domestic cane sugars and beet sugars provide only about 55 percent of the total sugar consumed in the United States. The remaining 45 percent of the sugar requirement is imported as raw cane sugar from foreign countries. The raw cane sugar (approximately 96 percent purity) is further purified in local sugar refineries in the United States (SIC 2062).

The production of raw sugar from sugar cane or refined sugar from sugar beets essentially involves the washing or cleaning of sugar cane or beets, extraction of sugar juice, precipitation and filtration of impurities (using lime and carbon dioxide), evaporation, crystallization, and drying of sugar crystals. Water is used in the process to wash the sugar cane or beets, to dissolve or extract sugar, and for cooling purposes.

The manufacture of sugar from sugar beets produces beet pulp and molasses as by-products. The beet pulp is pressed and dried for use as animal feed. The molasses, containing soluble non-sugars and some sugar, either is sold or is used in the Steffen Process to recover additional sugar. The Steffen Process involves the treatment of molasses with lime to recover additional sugar for recycle to the process. Wastewaters are typically added to the beet pulp and then dried, and sold as animal feed. A recent survey of 14 plants using the Steffen Process indicates that 5 plants use the Steffen Process waste to produce monosodium glutamate, while the others concentrate and dry the waste with beet pulp for use as animal feed (1). A modification of the Steffen Process, with barium hydroxide in place of the lime, is also used by some beet sugar plants (2,3).

The production of refined sugar from raw cane sugar involves washing the raw sugar to remove the molasses film from the sugar crystals, solution of the washed sugar, clarification of the solution by phosphoric acid-lime precipitation, carbonation, and/or pressure filtration, decolorization of the solution using powdered or granular carbon, bone char or resins, and evaporation of the clarified and decolorized solution to yield crystalline sugar.

The primary uses of water are to wash the decolorizing adsorbent and to serve as a cooling and condensing medium in the evaporating processes. The first use produces an effluent containing BOD and frequently suspended solids (waste filter aid). The second use leaves the water essentially unchanged except for an increase in temperature.

The principal by-product of the process is refinery molasses which is now sold for animal feeding purposes. Spent filter aid is generally sent to authorized dump sites. Waste bone char is sold to dealers for a variety of uses such as poultry feeding.

Because of the similarity of the wastewaters from the sugar industry, there are no separate pretreatment sub-groups for this industry.

2. Industrial Practices

The following industrial practices can significantly affect the wastewater characteristics.

The production of cane sugar involves by-products such as residual sugar cane fibers and blackstrap molasses. The residual fibers are generally used as fuel or in the production of fiberboard and paper products; the blackstrap molasses is recovered and sold as such. No additional waste loads result from the recovery or reuse of by-products (4,5).

The pulp press liquor and evaporator condensates can be recycled for use in the flume-washing operation.

3. Wastewater Characteristics

The characteristics of the process wastewaters from the industry are shown in Table D-7-1. Sugar plants generally operate 24 hours a day, but because of the nature of the raw materials (sugar cane and sugar beets), the domestic sugar industry operates seasonally from 60 to 100 days a year. The sugar refineries processing domestic and imported raw sugar can operate year-round. The sugar plants generate wastewater on a continuous basis during operational periods. However, the characteristics of the wastewater may fluctuate widely, becuase of variations in sugar content of the raw materials at different periods of the season. The variations in sugar content of raw materials are caused either by changes in weather conditions or in the storage of raw material (sugar cane or beets). In addition, hourly variations in wastewater characteristics may result from spills and leaks of sugar juice and from equipment cleanups.

The process wastewaters originate from the following operations in the production of raw cane sugar and refined beet sugar:

1. Flume washing
2. Lime cake or slurry
3. Evaporator condensates
4. Spills, leaks, and floor washing

Process wastewaters originate from the following unit operations in the refining of raw cane sugar:

1. Disposal of waste filter aid, carbonate cake, phosphoric acid precipitation scums, etc.

2. Washing of bone char and/or regeneration and reusing of resins.

3. Evaporator condensates.

The volume and characteristics of wastewater generated from the foregoing operations will depend on the degree of recycle practiced. The overall process wastewaters generally contain high concentrations of dissolved organics and suspended impurities, and are deficient in nutrients. The process wastewaters generated from each of the operations contain as major waste constituents BOD, COD, suspended solids, and heat. The wastewaters generated from sugar refineries are similar to those from sugar production from sugar cane and contain as major pollutants BOD_5 and suspended solids.

In general, the sugar industry wastewaters are amenable to treatment by joint treatment processes. The seasonal operation of some of the sugar plants and the widely-varying characteristics of the wastewaters should be taken into consideration in the design of joint treatment facilities.

4. Pretreatment

The pretreatment unit operations which may be necessary for various types of joint treatment facilities are shown in Table D-7-2.

Many sugar plants treat their wastewaters in holding lagoons, with controlled discharge of the lagoon effluent to municipal collection systems. The lagoons are effective for the removal of suspended solids and grit present in the wastewater. Typically, however, they are designed to remove only a small percentage of the BOD present in the raw wastewater (6).

The limited information available on the treatment of sugar industry wastes indicates that equalization (to reduce the fluctuations in organic loading), screening (to remove fibers), and clarification (to separate lime slurry and grit) would be needed as pretreatment before discharging these wastewaters to municipal collection systems. In addition, facilities for supplemental nutrients (nitrogen and phosphorus) at the joint treatment facility may be required.

Table D-7-1

Wastewater Characteristics
Sugar Industry

Characteristics	
Industrial Operation	SEASONAL[1]
Flow	Continuous-Variable
BOD	Low-EXT, HIGH
TSS	Low-EXT, HIGH
TDS	HIGH
COD	Low-EXT, HIGH
Grit	PRESENT
Cyanide	Absent
Chlorine Demand	HIGH
pH	Neutral
Color	Low-HIGH
Turbidity	PRESENT
Explosives	Absent
Dissolved Gases	Absent
Detergents	Absent
Foaming	Absent
Heavy Metals	Absent
Colloidal Solids	Low
Volatile Organics	Absent
Pesticides	Absent
Phosphorus	DEFICIENT
Nitrogen	DEFICIENT
Temperature	HIGH[2]
Phenol	Absent
Sulfides	Absent
Oil & Grease	Absent
Coliform (Fecal)	Absent
Coliform (Total)	PRESENT

[1] Industries which only process imported raw cane sugar operate year-round.

[2] Temperature higher than domestic wastewater. May affect design but not harmful to joint treatment processes.

NOTES: Characteristics which may require pretreatment or are significant to joint treatment plant design are shown in UPPER CASE.

Wastewater characteristics shown reflect all the industrial practices described under Section 2.

Pretreatment Unit Operations for the Sugar Industry

Suspended Biological System	Fixed Biological System	Independent Physical-Chemical System
coarse solids separation + equalization + grit removal + solids separation (lime slurry)^2	coarse solids separation equalization + grit removal + grit removal + solids separation (lime slurry)^2	coarse solids separation + grit removal + solids separation (lime slurry)^2

---

[1] Equalization may not be necessary, depending on specific physical-chemical processes used.

[2] Grit removal and solids separation for lime slurry may be combined.

REFERENCES

1. "State-of-Art, Sugarbeet Processing Waste Treatment," Water Pollution Control Research Series, 12060 DSI 7/71, Environmental Protection Agency, Washington, D.C. (1971).

2. Force, S.L., "Beet Sugar Factory Wastes and Their Treatment - Primarily the Findley System," *Proc. 17th Ind. Waste Conf.*, Purdue University, 116-135 (1962).

3. Rogers, H.G., and Smith, L.H., "Beet Sugar Waste Lagooning," Proc. 8th Ind. Waste Conf., Purdue University, 136-147 (1953).

4. Biglane, K.E., "Some Current Waste Treatment Practices in Louisiana Industry," *Proc. 13th Ind. Waste Conf.*, Purdue University, 12-20 (1958).

5. "Industrial Wastewater Control," (Ed.) Gurnham, C.F., Academic Press, New York (1965).

6. Kalda, D.C., "Treatment of Sugar Beet Wastes by Lagooning," *Proc. 13th Ind. Waste Conf.*, Purdue University, 126-139 (1958).

PETROLEUM REFINING INDUSTRY

1. Industry Description

This industry includes Standard Industrial Classification (SIC) 2911. This classification includes those establishments primarily engaged in producing gasoline, kerosine, fuel oils, residual fuel oils, lubricants, and other products through distillation of crude oil, cracking, or other processes. Petroleum refining is a combination of several interdependent processes and operations, many of which are highly complex. There are at least twenty separate processes fundamental to the operation of a refinery producing the full spectrum of products from crude oil.

The major operations within a refinery include: crude oil storage; desalting; fractionation by pressure, atmospheric and vacuum distillation; thermal and catalytic cracking; reforming; polymerization; and alkylation. Other incidental operations, generally involving separation and finishing of the products to specifications, include acid treatment of lubricating oil stocks, sweetening of gasoline, extraction, and stripping. Storage of crude oil to provide adequate working supplies and to equalize process flow involves the separation of water and suspended solids from crude oil

The first major operation in a refinery is the crude oil desalting process for removing inorganic salts and suspended solids from the crude oil prior to fractionation. Water is used in the desalting process as a sequestering agent.

The crude oil after desalting is generally passsed through atmospheric and/or vacuum distillation to separate light overhead products (C_5 and lighter), side-stream distillates, and residual crude oil. Steam is used in this process, and the steam condensate from the overhead accumulation is discharged as wastewater.

The heavy fractions removed during the crude oil fractionation and distillation process can be cracked using either thermal, catalytic, or hydrocracking processes to yield light oil fractions such as domestic heating oil. The low-octane fractions obtained from the foregoing processes can be converted to yield high-octane gasoline blending stock by reforming, polymerization, and/or alkylation processes. The reforming converts naphthas to finished high-octane gasoline. Reforming is a relatively clean process producing a low volume of dilute wastewater. The polymerization process produces wastewaters containing sulfide, mercaptans, high pH materials, and nitrogen compounds. Phosphoric acid or sulfuric acid is used in the polymerization process and generates solid wastes. The alkylation process uses a sulfuric acid or hydrofluoric acid catalyst to convert isoparaffins and olefins into high-octane motor fuel. Solvent refining is used in a refinery to extract lubricating oil fractions and aromatics from feedstocks containing various types of hydrocarbons.

A more detailed description of the individual petroleum refining processes is included in the "Industrial Waste Profile" published by the Federal Water Pollution Control Administration (now EPA) (1).

2. Industrial Practices

The petroleum refining industry uses very large quantities of water for process and cooling purposes. Approximately 90 percent of the water used in refineries is for cooling purposes. Lesser water uses include: steam generation (boiler-feed), direct processing, fire protection, and sanitary uses. Steam is used in stripping and distillation processes, where it comes in contact with petroleum products, thereby contributing to the total wastewater flow from refineries.

Oily process wastes and oil-free wastes are collected separately in some refineries so that the oily wastes can be treated for oil removal before mixing with other waste streams.

The spent caustics and spent acids are generally collected and sold or disposed by other means. Few refineries neutralize these wastes for discharge, to the wastewater collection system.

The sour water (condensates from various fractionation units) containing sulfides and ammonia is generally steam or air-stripped before being discharged to the sewer lines. A survey of petroleum refining industries in 1967 indicates that approximately 85 percent of the refineries strip the sour water before discharging to sewer lines. Depending on the pH of the sour water, the stripping can reduce the sulfide and ammonia concentrations in the final effluent.

In general, the in-plant control methods employed by the industry (sour-water stripping, spent-caustic neutralization and oxidation, slop oil recovery, etc.) will determine the final effluent characteristics and the level of pretreatment required for discharge to municipal collection system.

The technological advances in the refining process have resulted in increasing amounts of by-product recovery and a reduction in wastewater loading. Other advances in water usage and cooling water recirculation have also resulted in the reductions in volume of wastewater discharged per unit volume of crude oil processed. It has been reported that the total effluent from older, typical, and newer refineries are approximately 250,100 and 50 gal./bbl of crude oil respectively.

The following specific in-plant practices are frequently employed:

a. Sour-condensate stripping is used to remove sulfides (as hydrogen sulfide, ammonium sulfide, and polysulfides) before the wastewater enters the sewer. The sour water is usually treated by stripping with air, stream, or flue gas. Hydrogen sulfide released from the wastewater can be recovered as sulfuric acid or can be burned in a furnace. Hydrogen sulfides at concentrations in the range of 10 to 15 mg/L can cause upsets in biological treatment plants (4), and removal of sulfides from the sour water by stripping would prevent such upsets.

b. Spent caustic neutralization is applied to both phenolic and sulfidic waste streams, but oxidation of spent caustics is limited to sulfide waste streams, since phenols inhibit the oxidation of sulfides in spent caustics.

c. Spent acids (generally sulfuric) can be recovered for reuse or sold to acid manufacturers, thereby avoiding their discharge to sewer systems. Spent catalysts such as aluminum chloride and phosphoric acid can either be regenerated for reuse or disposed of as landfill.

3. Wastewater Characteristics

The characteristics of the process wastewaters from the industry are shown in Table D-8-1. Practically all petroleum refineries use gravity oil separators to recover free oil from process effluents. The effluents from gravity oil separators are therefore used to define the wastewater characteristics in the table.

The petroleum refineries operate on a continuous basis throughout the year except for separate process shutdowns for preventive maintenance and equipment repair and replacement. Many refineries have a segregated wastewater collection system, with separate subsystems for clean and polluted waste streams. The 'clean' waters may include pollution-free cooling waters, boiler blowdown, and cooling tower blowdown.

The characteristics of wastewater drawn from storage tanks will depend on the quality of the crude oil stored and may contain dissolved inorganics, oil, and suspended solids. The steam condensate from the overhead accumulator can be characterized as having oil, sulfides, mercaptans, and phenol. If barometric condensers are used in vacuum distillation, the condenser water will have very stable oil in emulsion. However, if the barometric condensers are replaced by surface condensers, the condenser water will be essentially free of oil.

The major wastewater from the alkylation process is the spent caustic from the neutralization of the hydrocarbon stream from the reactor. Even though the spent acids are recovered as salable by-product, leaks and spills of acid catalysts could reach the sewer lines. The major pollutants from the solvent refining processes include solvents such as phenols, glycols, and amines. Other processes for the manufacture of waxes and asphalt, and for finishing and blending of gasoline, produce relatively low volumes of dilute wastewater.

In general, the most significant process wastewaters from petroleum refining are: crude oil desalting waste, storage tank draw-off, steam condensates, spent caustics, spent acids, product losses, and leaks and spills of solvents used in extraction processes. The process wastewaters, which come in direct contact with petroleum hydrocarbons, contain free and emulsified oil, sulfides, phenols, ammonia, BOD, COD, heavy metals, and alkalinity as major waste constituents.

The presence of oil (free and emulsified) in the wastewater could vary between 30 and 200 mg/L in the effluent from API gravity separators (3).

Refinery wastewaters generally are susceptible to conventional biological treatment methods after adequate pretreatment. In addition, phosphorus supplementation may be required in some cases to provide a nutrient-balanced system for biological treatment. This supplemental nutrient requirement will depend on the phosphorus content of the cooling tower blowdown and its inclusion in the process wastewater.

4. Pretreatment

The pretreatment unit operations for various types of joint treatment facilities are shown in Table D-8-2.

These pretreatment operations were developed primarily from information on separate treatment of these wastewaters and assume the following industrial practices:

a. Sour condensate stripping to reduce sulfides and/or ammonia

b. Spent-caustic neutralization

c. Spent-acid neutralization and recovery or disposal by other means

d. Separate collection and disposal of acid sludges, clay, and spent catalysts

e. Gravity separation of free oil from process effluents

Depending upon the in-plant control methods used within a refinery it may be necessary to add sulfide removal and neutralization to the pretreatment operations listed in Table D-8-2.

The oil concentration in the wastewater should be reduced to approximately 50 mg/L in order to insure trouble-free operation in secondary biological treatment facilities. In addition, the presence of oil in a municipal sewer would constitute a fire and explosive hazard. For this reason, sewer ordinances generally have prohibited the discharge of refinery wastewaters to municipal facilities. A 1967 survey indicates that only 1 to 2 percent of the refineries discharge their effluent to municipal treatment systems.

Even though the current practice is to treat refinery effluent on-site, it appears that joint treatment with domestic wastes has a potential for adoption. The heavy metals present in refinery effluents (As, Cd, Cr, Co, Cu, Fe, Pb, Ni, and Zn) are generally in such low concentrations that they would not be a problem for joint treatment. If heavy metals reduction should be required by effluent guidelines, provisions should be made for their removal before discharging to municipal systems. The biological sludge developed from refinery wastewaters can be thickened and dewatered by conventional methods (vacuum filters and centrifugation).

4. Pretreatment

The pretreatment unit operations which may be necessary for various types of joint treatment facilities are shown in Table D-8-2.

The technological advancements in the refining process have resulted in increasing amounts of by-product recovery and a concomitant reduction in wastewater loading. Other advances in water usage and cooling water recirculation have also resulted in the reductions in volume of wastewater discharged per unit volume of crude oil processed.

The most prevalent in-plant treatment methods are sour-water stripping, neutralization and oxidation of spent caustics, ballast water treatment, and slop-oil recovery. These measures substantially reduce the waste loadings and to a significant degree are required to protect subsequent treatment. In addition to these in-plant control methods, practically all of today's refineries use gravity oil separators to recover free oil from process effluents. For these reasons and because the data available on raw wastewater characteristics are limited, the effluents from gravity oil separators are used to define the wastewater characteristics from petroleum refineries.

Table D-8-1

Wastewater Characteristics

Petroleum Refining Industry

Characteristics	
Industry Operation	Year-Round
Flow	Continuous
BOD	Average[1]
TSS	Low
TDS	HIGH
COD	HIGH
Grit	PRESENT
Cyanide	Present
Chlorine Demand	High
pH	ACID -ALKALINE
Color	Low
Turbidity	Low
Explosives	PRESENT
Dissolved Gases	Present
Detergents	Low
Foaming	Absent
Heavy Metals	PRESENT
Colloidal Solids	Low
Volatile Organics	Present
Pesticides	Absent
Phosphorus	DEFICIENT[2]
Nitrogen	Adequate
Temperature	HIGH[3]
Phenol	HIGH
Sulfides	HIGH
Oil & Grease	HIGH
Coliform (Total)	Low

[*] After gravity oil separation (API Separators).

[1] The refinery wastewaters have high COD/BOD ratios indicating the presence of biologically resistant organic chemicals.

[2] If cooling tower blowdown is also discharged with the process wastewater, phosphates may be present depending on water treatment.

[3] Temperature higher than domestic wastewater. May affect design but not harmful to joint treatment processes.

NOTES: Characteristics which may require pretreatment or are significant to joint treatment plant design are shown in UPPER CASE. Wastewater characteristics reflect all the Industrial Practices described in Section 2.

Table D-8-2

Pretreatment Unit Operations for the Petroleum Refining Industry[1]

Suspended Biological System	Fixed Biological System	Independent Physical Chemical System
Equalization + Coagulation - Solids Separation[2] + Neutralization	Equalization + Coagulation - Solids Separation[2] + Neutralization	Equalization + Coagulation - Solids Separation[2] + Neutralization

---

[1] Pretreatment Unit Operations Apply to API Separator Effluent

[2] Combined with Oil Removal to insure oil concentration below 50 mg/L

REFERENCES

1. "The Cost of Clean Waters, Volume III, Industrial Waste Profile No. 5, Petroleum Refining," U.S. Department of the Interior, FWPCA, (1967).

2. Nemerow, N.L., "Theories and Practices of Industrial Waste Treatment," Addison-Wesley Publishing Company, Inc., Reading, Mass. (1963).

3. Beychok, M.R., Aqueous Wastes from Petroleum and Petrochemical Plants", John Wiley and Sons, New York, (1967).

4. "Petroleum Refining Effluent Guidelines", Environmental Protection Agency, Washington, D.C. (Unpublished)

MEAT PRODUCTS INDUSTRY

1. Industry Description

This industry includes Standard Industrial Classification (SIC) Nos. 2011, 2013, 2014, and 2094.

These classifications include slaughterhouses, packinghouses, processing plants (beef, poultry, hog, and sheep), and rendering plants.

Live animals are usually held in holding pens for less than one day prior to slaughter. In the killing area, the animals are slaughtered and the carcasses drained of blood. The processes of skinning, defeathering or dehairing, and eviscerating follow the slaughtering of the animals. Depending on the desired product, carcasses may be cut into smaller pieces, e.g. hogs are cut into parts such as hams, sides, loins, and shoulders. These parts may be further processed (e.g. smoked or pickled), or they may be shipped directly to wholesalers without further processing.

Because of the similarity of the wastewaters from meat products industry, there are no separate pretreatment subgroups for this industry.

2. Industrial Practices

The following industrial practices can significantly influence the wastewater characteristics:

Sanitation Requirements

Unlike most other industries, the food industry is required to maintain strict sanitary conditions, which limits the amount of process wastewaters that can be recycled. The industry practices in-plant recovery (e.g. blood or grease) to reduce wastewater strength. In most plants, blood is collected and subsequently processed. The recovery of blood represents an in-plant practice which is extremely desirable since whole blood represents a BOD concentration of over 150,000 mg/L (1).

In addition, the dry handling of such wastes as manure and bedding materials from holding pens, paunch manure from eviscerating, and meat cuttings and trimmings will significantly reduce the quantity of waste materials discharged to the sewers. Implementation of these practices will affect the concentration and quantity of waste constituents, but not the quantity of wastewater.

Rendering

Rendering is a major unit process where in-plant modifications can significantly influence the pretreatment considerations. Wet and dry rendering are two subprocesses presently used within the industry. In the wet process, the meat by-products in a batch tank are cooked by direct injection of steam. Dry rendering uses only heat, and little wastewater is produced. In wet rendering, the solids in the water phase are screened out, and the remaining tank water may be evaporated or sewered. The tank water is a major source of organic pollution, when sewered, and has a BOD value of approximately 45,000 mg/L (2). Evaporation of wet-rendering tank water and the installation of entrainment separators on barometric condensers may reduce the need for pretreatment of wet-rendering process wastewaters.

Wastewater Segregation

Wastewater originating within a meat products plant will generally be made up of wastewater from the operations, sanitary wastes, and wastewaters from auxiliary sources (e.g. cooling water from ammonia condensers in the refrigeration systems). Many large plants providing their own complete or partial treatment have found it economical to segregate wastewaters into blood, clean water, manure-free water, and manure waters.

3. Wastewater Characteristics

The characteristics of wastewaters from the meat products industry are shown in Table D-9-1. The meat products industry is a year-round operation with daily operation on an intermittent basis. Plants usually shut down daily for an extensive clean-up period following the processing period. This practice results in the generation of intermittent wastewater flows.

Each plant may have a number of operations, depending on the products and degree of processing. However, the wastewaters generated from any meat products plant can be characterized as containing high concentrations of BOD, COD, TSS, TDS, and grease. Washdown of holding pens, mainly to remove manure and urine, will add to the BOD and suspended solids concentrations.

The processes of skinning, defeathering or dehairing, and eviscerating are sources of BOD, grease, and suspended solids. The disposal of paunch manure and the washing of carcasses during eviscerating are particular operations which generate substantial pollutants. The processing of hogs and fowl produce a floating solids problem caused by hair and feathers.

Dressing and processing operations are minor wastewater sources compared to the slaughterhouse operations. Wastewaters from these operations contain grease and solids originating from equipment washdown and product losses. Druing these operations, various trimmings, fat, and fleshings are produced

Considerations in the joint treatment of meat product wastewaters with domestic wastes are the high chlorine demand, the presence of surface-active agents, fecal coliform, intermittent flows, and the high septicity potential due to the high organic content of meat product wastewaters. In general, meat product wastewaters are amenable to either biological or chemical treatment.

4. Pretreatment

The pretreatment unit operations which may be necessary for various types of joint treatment processes are shown in Table D-9-2.

In addition to screening and free-floating grease removal, various in-plant control practices, such as blood recovery, and separate handling of paunch manure as solid waste would greatly reduce the waste constituents in process wastewaters (3).

When the ratio of meat product wastewater to domestic wastewater is over 50 percent, pretreatment should include equalization to reduce organic and hydraulic fluctuations. The equalization basin should be aerated to prevent septic conditions.

TABLE D-9-1

Wastewater Characteristics
Meat Products Industry

Characteristics	Meat Products
Industry Operation	Year-round
Flow	INTERMITTENT[1]
BOD	HIGH-EXT. HIGH
TSS	HIGH
TDS	HIGH
COD	HIGH - EXT. HIGH
Grit	Absent
Cyanide	Absent
Chlorine Demand	HIGH
pH	Neutral
Color	HIGH
Turbidity	High
Explosives	Absent
Dissolved Gases	Absent
Detergents	Present
Foaming	Absent
Heavy Metals	Absent
Colloidal Solids	HIGH
Volatile Organics	Absent
Pesticides	Absent
Phosphorus	Present
Nitrogen	Present
Temperature	Normal-High[2]
Phenol	PRESENT[3]
Sulfides	Absent
Oil and Grease	PRESENT
Coliform (Fecal)	PRESENT

---

[1] Wastewater flow is intermittent over the day or week.

[2] Temperature equal to higher than domestic wastewater; may affect design but not harmful to joint treatment processes.

[3] Phenols may be present in sanitizers used for clean-up.

NOTES: Characteristics which may require pretreatment or are significant to joint treatment plant design in UPPER CASE.

Wastewater characteristics shown reflect all industry practices described in Section 2.

TABLE D-9-2

Pretreatment Unit Operations for the Meat Products Industry

Suspended Biological System	Fixed Biological System	Independent Physical-Chemical System
Coarse Solids Separation + Grease Removal[2]	Coarse Solids Separation + Grease Removal[2]	Coarse Solids Separation + Grease Removal[2]

---

[1] Assumes in-plant recovery and separate handling of blood, manure, and paunch manure.

[2] Only free-floating oil and grease.

REFERENCES

1. "The Cost of Clean Water, Volume III, Industrial Profile No. 8 - Meat Products," Federal Water Pollution Control Administration, Washington, D.C., (September 1967).

2. "Industrial Waste Study of the Meat Products Industry", Contract No. 68-01-0031, Environmental Protection Agency, Washington, D.C., (unpublished).

3. "Industrial Wastewater Control", (Edited by) Gurnham, C.F., Academic Press, New York (1965).

1. Industry Description

This industry includes Standard Industrial Classification (SIC) 2041, 2044, and 2046. These classifications include milling flour or meal from grains, by either dry or wet processes.

The major grain milling establishments process corn, wheat or rice. Dry corn milling involves grinding and processing corn for the production of corn meal, flour, grits, and related products. Wet corn milling involves the separation of corn into several components such as starch, syrup, animal feeds, and various other products. Wheat milling generally uses a dry cleaning process. Par-boiling of rice is a wet process for boiling rough rice to force nutrients in the bran into the grain. The par-boiled rice is then milled to remove the inedible hull and the bran.

Because of the similarity of the wastewaters from the various segments of the grain milling industry, there are no separate pretreatment sub-groups for this industry.

2. Industrial Practices

The following industrial practices can significantly influence pretreatment.

Dry Corn Milling

The smaller plants use dry cleaning processes and produce only ground whole corn meal. The large plants, however, wash the corn prior to tempering and milling, to produce a variety of products. Water used to wash the corn is separated in centrifuges. The spent wash water, which constitutes the major wastewater source in a dry grain milling operation, is generally screened before being discharged to the sewers, and the screenings are recovered to prepare animal feeds. If corn oil is also produced (only in larger mills), steam and cooling water will be required to separate the oil from the solvent by evaporation. As a result, auxiliary wastewaters from water treatment, boiler blowdown, and cooling water will be discharged from mills producing corn oil.

Wet Corn Milling

The dry cleaned corn is steeped first in circulating water containing SO_2 for 30 to 40 hours. The light steep water is removed and concentrated by evaporation for use in preparing animal feeds. The evaporator condensates and starch filtrates constitute major wastewater sources from this industry. Small quantities of wastewater are added to the above source from equipment cleaning and washing operations. The starch slurry remaining after the separation of hulls, fiber, and germs is either used as starch or converted to syrup. The conversion of starch to acids. Even though the conversion of starch slurry to syrup and sugars (dextrose, lactic acid, etc.) generates large quantities of wastewater, these are generally reused for steeping corn and therefore cause only small quantities of wastewater to be discharged.

Wheat Milling

The dry process for milling and cleaning wheat produces no significant quantities of process wastewater. Only 5 percent of the wheat mills in the United States use water for cleaning wheat, and these wastes are discharged to municipal sewers. The manufacture of bulgur may produce a wastewater stream if the water is drained from bulgur wheat. However, most mills vent the moisture to the atmosphere during the drying and therefore do not produce any liquid wastes. In general, most grain mills processing wheat do not generate any liquid wastes,and those that employ wet cleaning of wheat discharge the wastewaters to municipal collection systems. Only five mills (estimated) in the United States make wheat starch from wheat flour. The wastewater from wheat starch production is similar to those from corn starch preparation (1).

Rice Milling

Rice milling generates wastewater only from the par-boiling operation. The spent cooling water is the principal wastewater generated from rice milling operations. Auxiliary wastewaters in rice milling industry result from water softening and boiler blowdown operations. The process wastewater (spent cooking liquor) is usually discharged to a municipal collection system.

3. Wastewater Characteristics

The characteristics of the wastewaters from the grain milling industry are shown in Table D-10-1. Most grain mills generate wastewater with similar pollutants and treatability characteristics.

Grain mills discharge wastewater varying in concentration and flow. Most mills operate 5 to 7 days per week, and 24 hours/day, and the operations are continuous batch-type. As a result, the wastewater quantity and characteristics are subject to hourly and daily variations. In addition, the starch-syrup plants may use different grains and product mixes at various times, thus contributing to the variations in wastewater volume and loading. the wastewater is generally rich in carbohydrates. However, nutrient addition may be required for specific cases.

The grain milling industry generates wastewater from wet cleaning, oil extraction,and starch and syrup manufacturing operations. Depending on the product mix and the type of grain used (corn, wheat, or rice), the wastewater characteristics vary widely within the industry. In general, the wastewaters constituents include: COD, BOD, suspended solids, heat, and acidity. The BOD and COD of the wastewater are attributed primarily to the presence of starch, carbohydrates, and proteins (1,2).

4. Pretreatment

The pretreatment unit operations which may be necessary for various types of joint treatment facilities are shown in Table D-10-2. The level of pretreatment required will depend on the ability of the joint treatment facility to absorb shocks of varying wastewater volume and loading (3). Wastewaters resulting from starch production are slightly acidic (pH 4 to 5) and therefore may require neutralization prior to discharging to municipal systems (4).

TABLE D-10-1

Wastewater Characteristics
Grain Mill Industry

Characteristic	
Industry Operation	Year-Round
Flow	CONTINUOUS
BOD	HIGH- EXT. HIGH
TSS	Low-EXT. HIGH
TDS	High
COD	HIGH- EXT. HIGH
Grit	Present
Cyanide	Absent
Chlorine Demand	High
pH	ACIDIC-ALKALINE
Color	Absent
Turbidity	Present
Explosives	Absent
Dissolved Gases	Absent
Detergents	Absent
Foaming	Absent
Heavy Metals	Absent
Colloidal Solids	Present
Volatile Organics	Low
Pesticides	Absent
Phosphorus	Low-Adequate
Nitrogen	Low-Adequate
Temperature	High
Phenol	Absent
Sulfides	Absent
Oil and Grease	Absent
Coliform (Total)	Present

1 Higher temperature than domestic wastewaters. May effect design but not harmful to joint treatment processes.

NOTES: Characteristics which may require pretreatment or are significant to joint treatment plant design are shown in UPPER CASE.

Wastewater characteristics shown reflect all industrial practices described in Section 2.

Table D-10-2

Pretreatment Unit Operations for the Grain Mill Industry

Suspended Biological System	Fixed Biological System	Independent Physical/Chemical System
Coarse Solids Separation + Equalization + Neutralization	Coarse Solids Separation + Equalization + Neutralization	Coarse Solids Separation + Equalization + Neutralization

REFERENCES

1. "Industrial Waste Study Report - Grain Milling Industry", Environmental Protection Agency, Washington, D.C., (unpublished).

2. Ling, J.T., "Pilot Investigation of Starch - Gluten Waste Treatment", Proceedings 16th Industrial Waste Conference, Conference, Purdue University, 515-525 (1967).

3. Willenbrink, R.V., "Waste Control and Treatment by a Corn and Soybean Processor", Proceedings 22nd Industrial Waste Conference, Purdue University, 515-525 (1967).

4. Jeyfriend, C.F., "Purification of Starch Industry Wastewater", Proceedings 23rd Industrial Waste Conference, Purdue University, 1103-1119 (1968).

1. Industry Description

This industry includes Standard Industrial Classifications (SIC) 2033, 2034, 2035, and 2037. These industrial classifications include the processing of fruits and vegetables, including cleaning, sorting, sizing, peeling, stabilizing, and final processing.

Because of the similarity of the pollutants significant to pretreatment of wastewaters from the various segments of the fruit and vegetable industry, there are no separate pretreatment sub-groups for this industry.

Washing is a unit process integral to all fruit and vegetable processing. Wash water is used to remove dirt, insects, and residual pesticides. Root crops, such as potatoes and carrots, have greater amounts of dirt than fruits and vegetables grown above ground.

Sorting is performed (usually manually) to remove inferior fruits and vegetables, which are then directed into end products which are not sensitive to appearance. Conveyance between unit processes is often done in flumes to prevent damage to the product and to minimize the deteriorating effect that air has on many products, e.g., apples turn brown in the presence of air.

Separation of fruits and vegetables into desired size ranges is generally performed by using mechanical equipment.

Peeling, when required, is accomplished by either mechanical abrasion, by chemical (lye) treatment, or by steam. An experimental method of dry caustic peeling has been evaluated successfully for pears, peaches, potatoes and beets (1). Mechanical abrasion utilizes contoured knife peelers adjusted to maximize product yield for the particular size of product being processed. Steam and hot lye peeling depend on water sprays to remove the softened skin. Hot lye solutions may be sewered as frequently as after each work shift (2).

The peeling process represents a substantial source of pollutants, principally soluble, including: sugars, starches, and carbohydrates leached from the fruits and vegetables; and insoluble waste solids. The form of the final product is also a factor in the relative quantity of pollutants generated. For example, fruits are generally marketed in a whole, halved, quartered, or diced form. The greater the exposed area (diced vs. halved), the greater the extent of leaching of pollutants from the product.

Stabilizing of the fruit or vegetable to preserve its quality may be accomplished by blanching or pasteurization. Blanching is accomplished with steam, to expel air and inactivate enzymes which would cause color change and wilting. Generally, only juices and some commodities are pasteurized to prevent deterioration.

Fruit and vegetable processing can also include canning, frying, freezing, or dehydration. Canning can also involve cooking, which is done in a pressurized steam cooker; thereafter, the cans are cooled with water before being labeled and packed in cartons.

2. Industrial Practices

The following industrial practices can significantly infl influence pretreatment:

Trimming and Peeling Wastes

Trimmings and other large solids should be handled as a dry solid waste and not sewered. This practice would affect the pretreatment screening requirements.

Wash Water Recycle

A closed wash water recycle system with separate grit disposal will generally preempt grit removal as a pretreatment requirement.

Peeling Process

The substitution of another peeling process for lye treatment may nullify the need for neutralization facilities for pH adjustment.

Washing Operation

Reduction of wastewater quantities is critical in order to obtain a minimal capital investment for pretreatment facilities. Counter-current flow during the washing operation has been credited with substantially reducing the overall volume of wash water. In addition, low-volume, high-pressure sprays have been successfully employed in various establishments.

3. Wastewater Characteristics

The characteristics of the wastewaters from the processing fruits and vegetables are shown in Table D-11-1. The

Fruit and vegetable industry is a seasonal operation, usually corresponding to the local growling season. Within this industry one particular cannery may process more than one fruit or vegetable, e.g. corn in summer and apples in the fall. In addition, apples and potatoes are stored under controlled temperature and humidity, with the overall effect of prolonging the industry operation. This industrial category can be classified as a continuous operation, with the exception of fruits and vegetables that are pickled or cooded. These latter processes are batch types. In general, the wastewaters from this industry are high in BOD, COD, TSS, and grit (3,4).

4. Pretreatment

The pretreatment unit operations which may be necessary for various types of joint treatment processes are shown in Table D-11-2. Water re-use and process equipment within each plant will dictate the pretreatment and subsequent treatability. In general, fruit and vegetable wastewaters are amenable to either biological or chemical treatment (5).

Design consideration in the joint treatment of vegetable and fruit wastewater with domestic wastes should include the high chlorine demand, presence of surface-active agents, nutrient deficiency, and pH variability. Pesticides may have ever been sprayed with a long-life pesticide. There is no substantial information at present on the measurable quantities of pesticides in the wastewaters.

TABLE D-11-1

Wastewater Characteristics
Fruit and Vegetable Industry

Characteristics	
Industrial Operation	SEASONAL
Flow	INTERMITTENT
BOD	Average-EXT. HIGH
TSS	Average-EXT. HIGH
TDS	Average-HIGH
COD	Average-EXT. HIGH
Grit	PRESENT
Cyanide	Absent
Chlorine Demand	Average-HIGH
pH	ACID-ALKALINE[1]
Color	Present (HIGH[2])
Turbidity	High
Explosives	Absent
Dissolved Gases	Absent[3]
Detergents	PRESENT
Foaming	Absent
Heavy Metals	Absent
Colloidal Solids	Average
Volatile Organics	Absent
Pesticides	Absent-Present
Phosphorus	DEFICIENT
Nitrogen	DEFICIENT
Temperature	Normal-High[4]
Phenol	Absent
Sulfides	Absent
Oil & Grease	Absent
Fecal Coliform	Absent

---

1. Fruit and tomato wastes are generally acidic; however, the pH of the wastewater is affected by the peeling process, e.g., lye peeling.
2. Beet processing wastewaters are characterized by a red color.
3. Free SO_2 may be dissolved in maraschino cherry brine.
4. Temperature equal to or higher than domestic wastewater. May affect design but not harmful to joint treatment processes.

NOTES: Characteristics which may require pretreatment or are significant to joint treatment plant design are shown in UPPER CASE.

Wastewater characteristics shown reflect all the industrial practices described in Section 2.

TABLE D-11-2

Pretreatment Unit Operations for the Fruit and Vegetable Industry

Suspended Biological System	Fixed Biological System	Independent Physical Chemical System
Coarse Solids Separation + Grit Removal + Neutralization[1]	Coarse Solids Separation + Grit Removal + Neutralization[1]	Coarse Solids Separation + Grit Removal + Neutralization[1]

---

[1] Neutralization is dependent on commodity and peeling process employed.

REFERENCES

1. Industrial Waste Study - Canned and Frozen Fruits and Vegetables, Contract No. 68-01-0021, Environmental Protection Agency, Washington, D.C. (unpublished).

2. "Industrial Wastewater Control", (Edited by) Gurnham, C.F., Academic Press, New York (1965).

3. "Utilization of Cannery Fruit Waste by Continuous Fermentation", Bulletin No. 207, Washington State Institute of Technology, Pullman, Washington (March 1950).

4. "Treatment of Citrus Processing Wastes", Water Pollution Control Research Series 12060, Environmental Protection Agency, Washington, D.C. (1970).

5. "The Cost of Clean Water, Volume III, Industrial Waste Profile No. 6 - Canned and Frozen Fruits and Vegetables", Federal Water Pollution Control Administration (June 1967).

BEVERAGES INDUSTRY

1. Industry Description

This industry includes Standard Industrial Classification (SIC) 2082, 2083, 2084, 2085, 2086, and 2087.

These industrial classifications include all establishments engaged primarily in the manufacture of malt, malt beverages (ale, beer, and malt liquors), wines (table wine, dessert wine, and brandy), distilled spirits, bottled and canned soft drinks, and flavoring extracts and syrups.

The products described above can be classified under two major groups according to their basic manufacturing processes as:

1. Fermentation Products (beer, wine, distilled spirits, malt)
2. Extraction Products (soft drinks, flavors, and extracts)

The fermentation products are made from grains or fruits, while the extraction products are made from flavor substitutes of oils such as cocoa, vanilla, and orange oil. The fermentation products derived from grains are manufactured by cooking the grains, fermenting the cooking liquor with a yeast culture, and separating the fermented alcohol by clarification and filtration.

The manufacturing processes used for the production of flavoring extracts and syrups are proprietary in nature. The basic processes for the recovery of natural flavoring can be listed as follows:

1. Steam distillation and petroleum ether extraction (essential oils).

2. Expression (hydraulic pressing) and petroleum ether extraction (fruit syrup).

3. Expression and evaporation (jams).

4. Alcoholic extraction of vanilla and other tissue.

The soft drink bottling and canning plants use flavor extracts and purchased syrups. The bottling and canning process involves bottle washing and sterilizing, mixing of flavor extracts and syrup, carbonation, and filling.

The pretreatment sub-groups for this industry are as follows:

Malt, malt beverage, and distilled spirits (except industrial alcohol).

Wine and brandy.

Bottled and canned soft drinks, and flavors and syrups.

2. Industrial Practices

During the brewing and fermentation process, malt and hops are added to convert starch to sugar and to incorporate a bitter taste to the product. Water is used in the process for cooking, cooling, container washing and other miscellaneous uses. Both solid wastes and liquid wastes are generated in the process. Spent grains, excess yeast, and spent hops are the solid wastes, and are generally hauled away or dried for livestock and poultry feed. The only variation of this type of disposal is where certain small distilleries manufacturing distilled wine or spirits, the stillage is discharged with other liquid wastes. Liquid process wastes result from fermentation, aging, filtration and evaporation, and washing and clean-up operations (1,2). Liquid wastes are also discharged from auxiliary operations such as cooling, boiler blowdown, and water softening.

The fermentation process results in the generation of "lees", which is a mixture of wine, yeast ceels, and other sediment. The lees is considered a liquid or semi-liquid waste, which is either discharged directly to the sewer or recovered in the case of large wineries. In order to improve the quality of the wine, the fermented liquid is often processed by a sequence of racking, filtration, and fining operations. The wastes from racking (clarification) and filtration often produce a sludge containing significant quantities of wine. When these wastes are sewered, they add significantly to the BOD and solids concentration of the wastewater. Brandy is produced by distillation of wine and condensation of the overhead in order to obtain a beverage with high alcohol content. The stillage from such distillation is a very significant liquid waste (3,4).

The manufacture of flavoring extracts and syrups also generates both liquid and solid wastes. Solid wastes are the residues after extraction of flavors and syrups. Wastewaters from normal extraction operations are:

Fruit Expression:

1. Water used for washing fruits.
2. Hydraulic press clean-up.

Evaporation:

1. Evaporator condensate.
2. Kettle wash water.

Steam Distillation:

1. Boiler blowdown.
2. Bottoms from packed column.

The major wastewater sources in the bottling industry are the bottle washing and clean-up operations. Auxiliary wastewaters such as cooling, air conditioning, and boiler blowdown are also generated (5).

The predominant method of disposing of liquid wastes from beverage plants is by discharging to municipal sewerage systems. A typical plant collects all its wastewaters in a common sewer and discharges them to municipal sewers.

3. Wastewater Characteristics

The characteristics of process wastewaters from each pretreatment sub-group are shown in Table D-12-1.

The beverage industries generally operate throughout the year. However, the volume of waste production and the loading will vary with the season depending upon product demand. A recent survey of the malt beverage industry indicates that wastewater volume and load both peak during the summer months, and are lowest during the winter months. This is probably due to the scheduling of production in response to demand and usage.

Major considerations in the joint treatment of beverage wastewaters are the presence of large particulate matter in suspension and the fluctuations in hydraulic and organic loads. The follwing is a brief description of the wastewater from each pretreatment group:

1. Malt Beverages and Distilled Spirits

The wastewaters generated from the malt and malt beverages industries have as major constituents BOD, SS, pH and temperature. The waste solids from the malt house, and the excess yeast, spent grains, and spent hops from the malt beverages industry are disposed of either by hauling away or by on-site drying to make cattle feeds. If the spent wet grain is dried in the brewery, the spent grain liquid must be disposed of; generally, it is discharged to municipal sewers without pretreatment.

The distilleries produce wastewaters from cooking and fermentation of grains, the stillage or slops from distilling operations, and from washing and bottling operations. The stillage from the distilleries contain yeast, proteins, and vitamins. Depending upon the size of the plant, complete or partial recovery of stillage is practiced. The major constituents in distillery wastewaters include BOD, suspended solids, acidity, and heat.

2. Wine and Brandy

The wine and brandy industries produce wastewaters from crusher-stemmer, pressing, fermentation, clarification and filtration, distillation, and bottling operations. Brandy is manufactured by distillation of wine and, therefore, results in the generation of stillage or "still slop". The stillage is a very significant liquid waste in the manufacture of brandy. The wastewaters are high in organics and have the potential of introducing shock loads in joint treatment works (3).

3. Soft Drinks, Flavors, and Syrups

The wastewaters generated from the manufacture of flavor extracts and syrups are generally discharged to municipal sewerage systems without treatment. Very little work, if any, has been done to delineate the characteristics of the wastewater from this segment of the industry. The bottling and canning of soft drinks generate wastewaters primarily from bottle-washing operations. These wastes contain BOD, suspended solids, and alkalinity. Some bottling industries practice recirculation of final rinse water for pre-rinsing, thereby reducing the volume of wastewater discharged to the sewers (5).

4. Pretreatment

Available information in the literature indicates that pretreatment in the form of screening, grit removal, and equalization are practiced by some industries.

The pretreatment unit operations shown in Table D-12-2 are based upon total process wastewater discharge from all unit operations within the industry. The addition of auxiliary wastes (cooling, boiler blowdown, and water softening) will lower the strength of total effluent from the industry. In general, the wastewaters from the beverage industries are amenable to treatment by conventional processes, such as activated sludge and trickling filters. The pretreatment unit operations recommended in Table D-12-2 are based on the assumption that the following in-plant pollution control methods are practiced:

1. Hauling or drying of spent grains, hops, and stillage.
2. Separate solids-handling and disposal of crusher-stemmer and pressing wastes.

Spent grains, hops, stillage, crusher-stemmer, and pressing wastes can be characterized as solid wastes rather than liquid wastes. Therefore, it is desirable to collect them separately for disposal.

Wastes from the malt industry have been successfully treated even when they constitute 45 percent of the total flow and 76 percent of the total BOD loadings in joint treatment works (2). Similar results have been reported for the joint treatment of malt beverage wastewaters when they form 4.2 percent of the total flow and 25 percent of the total organic loading (2). These results suggest that in a well designed and well operated joint treatment works, the beverages industrial wastes are similar to domestic wastes, and that the ratio of industrial wastes to domestic wastes does not significantly influence the treatability characteristics of the combined waste. However, it may be necessary to provide supplemental nutrients (nitrogen and phosphorus) in joint treatment facilities.

TABLE D-12-1

Wastewater Characteristics

Beverages Industry

Characteristics	Malt Beverages and Distilled Spirits	Wine and Brandy	Soft Drinks Bottling[1]
Industry Operation	Year-round	SEASONAL	Year-round
Flow	INTERMITTENT-Continuous[2]	INTERMITTENT	INTERMITTENT
BOD	HIGH	HIGH-EXT. HIGH	Average to HIGH
TSS	Low to HIGH	Low to EXT. HIGH	Low to HIGH
TDS	High	High	Low to High
COD	HIGH	HIGH-EXT. HIGH	Average to HIGH
Grit	PRESENT	PRESENT	PRESENT
Cyanide	Absent	Absent	Absent
Chlorine Demand	No Data	No Data	No Data
pH	ACID-NEUTRAL	ACID-ALKALINE[3]	ALKALINE[3]
Color	Present	Present	Present
Turbidity	Present	Present	Present
Explosives	Absent	Absent	Absent
Dissolved Gases	Present	Absent	Present
Detergents	Present[4]	Present[4]	Present[4]
Foaming	Present	Present	Present
Heavy Metals	Absent	Absent	Absent
Colloidal Solids	Present	Present	Present
Volatile Organics	Present	Present	Present
Pesticides	Absent	Absent	Absent
Phosphorus	DEFICIENT	DEFICIENT	DEFICIENT
Nitrogen	DEFICIENT	DEFICIENT	DEFICIENT
Temperature	Normal-High[5]	High	Normal
Phenol	Absent	Absent	Absent
Sulfides	Absent	Absent	Absent
Oil and Grease	Absent	Absent	Absent
Coliform (Fecal)	Absent	Absent	Absent
Coliform (Total)	Present	Present	Present

---

[1] Pollutants characteristics represent only Bottling Industry; no data available for flavors and syrups.

[2] Malt beverages generate wastes on a continuous basis; distilled spirits waste flow will be cyclic.

[3] Alkaline pH due to caustic detergents used for bottle washing.

[4] Surface active agents are discharged primarily from bottle washing.

[5] Temperature equal to or higher than domestic wastewater; may affect design but not harmful to joint treatment processes.

NOTE: Characteristics which may require pretreatment or are significant to joint treatment plant design are shown in UPPER CASE.

Wastewater characteristics shown reflect the industrial practices described in Section 2.

TABLE D-12-2

Pretreatment Unit Operations for the Bevaerages Industry

Pretreatment Sub-Group	Suspended Biological System	Fixed Biological System	Independent Physical-Chemical System
Malt Beverages	Coarse Solids Separation + Grit Removal + Equalization + Neutralization	Coarse Solids Separation + Grit Removal + Equalization + Neutralization	Coarse Solids Separation + Grit Removal + Equalization + Neutralization
Wine and Brandy	Coarse Solids Separation + Grit Removal + Equalization + Neutralization	Coarse Solids Separation + Grit Removal + Equalization + Neutralization	Coarse Solids Separation + Grit Removal+ Equalization + Neutralization
Soft Drinks Bottling	Grit Removal + Neutralization	Grit Removal + Neutralization	Grit Removal + Neutralization

REFERENCES

1. "Industrial Waste Survey on Malt Liquor Industry", prepared for the Environmental Protection Agency by Aware, Inc., Nashville, Tennessee (unpublished).

2. "Industrial Waste Survey of the Malt Industry," prepared for the Environmental Protection Agency by Aware, Inc., Nashville, Tennessee (unpublished).

3. "Industrial Waste Survey of the Wine Industry," prepared for the Environmental Protection Agency by Aware, Inc., Nashville, Tennessee (unpublished).

4. "Industrial Waste Survey of Distilled Spirits Industry," prepared for the Environmental Protection Agency by Aware, Inc., Nashville, Tennessee (unpublished).

5. "A Report on Bottled and Canned Soft Drinks SIC 2086 and Flavoring Extracts and Syrups SIC 2087," prepared for the Environmental Protection Agency by Aware, Inc., Nashville, Tennessee (unpublished).

PLASTIC AND SYNTHETIC MATERIALS INDUSTRY

Industry Description

This industry includes Standard Industrial Classifications (SIC) No. 2821, 2823, and 2824. These classifications include the manufacture of plastic and synthetic materials, but not the manufacture of monomers, formed plastic products (other than fibers), and paint formulations. The manufacture of resins used in paints is also included.

Plastics and resins are chain-like structures known chemically as polymers. All polymers are synthesized by one or more of the following processes: bulk, solution, emulsion, and suspension. After polymerization, the products undergo separation, recovery, and finishing before being marketed.

There are numerous plastics and synthetics manufactured in this industry. For these guidelines, a national production volume of greater than 50 million pounds per year was selected as the criterion for inclusion of a polymer.

Based on the wastewater characteristics and treatability information, the industry is divided into the following pretreatment sub-groups:

Pretreatment Sub-Group	
1	Rayon Fibers Nylon Fibers
2	High- and Low-Density Polyethylene Resins
3	Urethane Resins Polyolefin Fibers Polyvinyl Acetate Resins Polyvinyl Alcohol Resins Polyester Fibers
4	Cellulosic Resins Cellophane Polypropylene Resins Cellulose Acetate Fibers Polyvinyl Chloride Resins Polystyrene ABS, SAN Resins Phenolic Resins Nylon Resins Polyacetal Resins Acrylic Fibers

2. Industrial Practices

The following industrial practices can significantly influence the wastewater characteristics.

Suspension Polymerization

In suspension polymerization, a monomer (e.g. vinyl acetate) is dispersed in a suspending medium consiting of a mixture of water and suspending agents such as polyvinyl alcohol, gelatin, etc. The suspension is heated, and polymerization occurs. The polymer is then separated in a centrifuge, washed, and dried in rotary driers. The centrate from the separation process may contain suspending agents, surface-active agents, catalysts, (e.g. benzoyl, lauroyl) and small amounts of unreacted monomer (1).

Emulsion Polymerization

Emulsion polymerization consists of solubilization and dispersion of the monomer in a solvent (e.g., water, cyclohexane, or tetrahydrofuran) with the appropriate emulsifiers (e.g., soaps or surfactants). Before polymerization occurs, initiators such as persulfates, hydrogen peroxides, etc. are added. When polymerization is complete, the product is a milk-like latex of permanently dispersed polymer, from which the polymer particles are recovered, generally by spray drying or by coagulation and centrifugation.

Solution Polymerization

Solution polymerization relies on a solvent to dissolve the monomer and catalyst. After reaction, the polymer is precipitated using an antisolvent (e.g. n-hexane, methanol). The polymer is then filtered and dried.

Bulk or Mass Polymerization

Bulk or mass polymerization is different from the foregoing processes in that no carrier liquid is used. Therefore, there is generally little or no process wastewater associated with this process.

3. Wastewater Characteristics

The characteristics of the process wastewaters from the manufacture of plastic and synthetic materials are shown in Table D-13-1.

The plastic and synthetic materials industry is typically a continuous year-round operation. Because it is technically and economically advantageous, many firms manufacture several different, but related chemical products at one location. For example, a typical complex makes ethylene, polyethylene, sulfuric acid, ethyl chloride, ammonia, nitric-acid and phosphoric acid (2).

In group 1, the wastewater has relatively high BOD, COD, and TSS; heavy metals (Zn, Cu) and synthetic fiber losses. Group 2 wastewater has low BOD and COD, may be either acidic or alkaline, and has substantial amounts of oil and polymer particles. Group 3 is characterized as either having no process water or as having process wastewater containing virtually no pollutants. Group 4 wastewater has variable BOD and COD, may be either acidic or alkaline, and contains synthetic fibers. Discharge of faulty batches from synthetic fiber plants may introduce shock loads into the joint treatment facility.

Conditions significant in the design of joint treatment facilities include high chlorine demand, the presence of surface-active agents, high solids concentrations, and nutrient deficiency. The process diversity and complexity, as well as the proprietary nature of many of the process chemicals, require that the pretreatment be established on a case-by-case basis after thorough investigation.

4. Pretreatment

The pretreatment unit operations which may be necessary for various types of joint treatment processes are shown in Table D-13-2.

TABLE D-13-1
Wastewater Characteristics
Plastic and Synthetics Industry

Characteristics	Sub-Group 1	Sub-Group 2	Sub-Group 3	Sub-Group 3
Industry Operation	Year-Round	Year-Round	--[3]	Year-Round
Flow	Continuous-Variable	Continous		Continuous
BOD	HIGH	Low	Low	Average-HIGH
TSS	HIGH	Low	Low	Low-HIGH
TDS	HIGH	Low	Low	Low-HIGH
COD	HIGH	Low	Low	Average-HIGH
Grit	Absent	Absent	Absent	Absent
Cyanide	Absent	Absent	Absent	Absent
Chlorine Demand	HIGH	Low	Low	AVERAGE-HIGH
pH	ACID-BASIC	ACID-BASIC	Neutral	ACID-BASIC
Color	Low-Average	Low-Average	Low	Low-Average
Turbidity	High	Low	Low	Low-High
Explosives	Absent	Absent	Absent	Absent
Dissolved Gases	Absent	Absent	Absent	Absent
Detergents	Absent	Absent	Absent	PRESENT
Foaming	Absent	Absent	Absent	Absent
Heavy Metals	PRESENT	Absent	Absent	Absent
Colloidal Solids	HIGH	Low	Low	Average
Volatile Organics	Absent	Present	Absent	Present
Pesticides	Absent	Absent	Absent	Absent
Phosphorus	DEFICIENT	DEFICIENT	DEFICIENT	DEFICIENT
Nitrogen	DEFICIENT	DEFICIENT	DEFICIENT	DEFICIENT
Temperature	Normal-High	Normal-High	Normal-High	Normal-High
Phenol	Absent	Absent	Absent	Present
Sulfides	Absent	Absent	Absent	Absent
Oil and Grease	Absent	PRESENT	Absent	Absent
Coliform (Fecal)	Absent	Absent	Absent	Absent

[1] Products generally associated with little or no process wastewater

[2] Temperature equal to or higher than domestic wastewater. May affect the design but not harmful to joint treatment processes.

[3] See text page D-13-3

NOTE: Characteristics which may require pretreatment or are significant to joint treatment plant design are shown in UPPER CASE.

Wastewater characteristics shown reflect the industrial practices described in Section 2.

TABLE D-13-2

Pretreatment Unit Operations for the Plastic and Synthetic Materials Industry

Pretreatment Sub-Group	Suspended Biological System	Fixed Biological System	Independent Physical-Chemical System
1	Coarse Solids Separation + Neutralization + Chemical Precipitation (heavy metals)	Coarse Solids Separation + Neutralization + Chemical Precipitation (heavy metals)	Coarse Solids Separation + Neutralization + Chemical Precipitation (heavy metals)
2	Oil Separation[1] + Neutralization	Oil Separation[1] + Neutralization	Oil Separation[1] + Neutralization
3	Pretreatment Not Required	Pretreatment Not Required	Pretreatment Not Required
4	Coarse Solids Separation + Neutralization	Coarse Solids Separation + Neutralization	Coarse Solids Separation + Neutralization

[1] Oil separation required to reduce mineral oil (petroleum sources) concentration below 50 mg/L.

NOTE: Publicly owned treatment works must be protected from batch dumpings of faulty product materials.

REFERENCES

1. "Industrial Waste Study of the Plastic Materials and Synthetics Industry", Environmental Protection Agency Contract No. 68-01-0030, Washington, D.C., (unpublished).

2. "The Cost of Clean Water - Vol. III, Industrial Waste Profile No. 10 - Plastic Materials and Resins", Federal Water Quality Administration (October, 1967).

BLAST FURNACES, STEEL WORKS, AND ROLLING AND FINISHING

1. Industry Description

This industry includes Standard Industrial Classification (SIC) 3312.

This classification includes: pig iron manufacture; manufacture of ferroalloys from iron ore and from iron and steel scrap; converting pig iron, scrap iron, and scrap steel into steel; hot rolling; and cold finishing. Blast furnaces and by-product (or beehive) coke ovens are also included under this category. The complex and interdependent operations involved in a steel industry can be listed as follows:

a. Coke Works
b. Iron Works
c. Steel Works
d. Hot Forming
e. Cold Finishing

Significant quantities of water are used, both for processing and for cooling purposes. The steel industry generates greater volumes of wastewater than any other industry (1).

a. Coke Works

Coke is used in large quantities for the production of pig iron. Therefore, most large iron and steel manufacturing operations include the production of coke from coal. There are two methods generally used for the production of coke: 1) the beehive process; and 2) the by-product or chemical recovery process. The beehive process uses air in the coking oven to oxidize the volatile organics released from coal and to recover the heat for further distillation. The by-product or chemical recovery process is operated in the absence of oxygen, and the heat required for distillation is provided from external fuel sources. Today, the by-product process accounts for 99.9 percent of all metallurgical coke. Therefore, only the by-product or the chemical recovery process is described in detail.

In the by-product process, coal is heated in the absence of air to a temperature at which the volatile matter is driven off. At the end of coking cycle, the hot residual coke (2,000° F) is conveyed to a quenching station, where it is cooled with a spray of water. The off-gases from the coke oven are cooled in a cooling train, where tar and ammonia liquor separate out. The tar contains a large proportion of phenols removed from the furnace. The ammonia is generally recovered from the liquor in a still.

b. Iron Works

Iron is manufactured from iron ore (iron oxide) in blast furnaces, with carbon monoxide (from coke) as a reducing agent. The major impurity (silica) in the iron ore is removed from the blast furnace as molten slag, through the use of limestone.

c. Steel Works

Steel is manufactured from pig iron by adjusting the carbon content of the alloy to approximately 1 percent. The three principal steel-making units are the electric arc furnace, the open-hearth furnace, and the basic oxygen furnace. The basic oxygen furnace produces approximately 50 percent of the total steel produced in the United States (2).

All three methods use the same raw materials and produce similar wastes. Pure oxygen or air is used to refine the hot iron into steel by oxidizing and removing silicon, phosphorus, manganese, and carbon from the iron.

d. Hot Forming

The steel ingot obtained from the furnace is reheated to provide uniform temperature for further processing or hot forming. The ingot steel is generally processed in a blooming mill or slab mill to form plates, sheets, strip, skelp, and bars.

e. Cold Finishing

The cold finishing operations are used for the conversion of hot-rolled products to give desired surface, shape, or mechanical properties. These operations include pickling, cold rolling, tinplating, coating, shaping, and drawing to make various finished products.

Integrated iron and steel mills may operate many different subprocesses generating wastewaters of varying characteristics. There are, however, mills which are not integrated and which have only a few of the foregoing manufacturing operations.

The only two types of waste stream susceptible to joint treatment are the coke oven wastewaters and the pickling liquor. The other process wastes occur in such large quantities and contain only suspended impurities that it is more logical to treat them on-site and discharge directly to surface waters.

Consequently, the pretreatment sub-groups for this industry are:

Coke Works
Cold Finishing

2. Industrial Practices

The strong acid pickle liquor, containing iron salts of mineral acids, is usually collected separately for other means of disposal or for use in waste treatment plants. The acid salts of iron are useful either as a flocculent aid, as a precipitating agent for phosphorus removal, or as a neutralizing agent in waste treatment plants. Any such use should be investigated before discharging the spent pickle liquor as a waste stream. Recovery of strong acid pickle liquor for reuse is practiced in a limited number of cases for hydrochloric acid systems.

3. Wastewater Characteristics

The characteristics of the process wastewaters from various operations within the steel industry are shown in Table D-14-1.

The wastewaters generated in steel industries vary widely between operations and they are generally segregated for treatment. Some older steel mills, however, still have common collection systems for discharging the total plant flow. The steel industry operates throughout the year and generates wastewaters over a 24-hour day. The volume and characteristics of wastewater are subject to hourly variations from batch dumping of acid baths and still bottoms.

The major constituents present in the wastewater are phenol, cyanides, ammonia, oil, suspended solids, heavy metals (Cr, Ni, Zn, Sn), dissolved solids (chlorides, sulfates), acidity, and heat. The process wastewaters are generally treated on-site before disposal. Joint treatment of these wastes with municipal wastes is limited to small installations, which handle only approximately 5 percent of the overall steel industry. This is probably due to the excessive volumes of wastewater (12,000-25,000 gpm) generated by large integrated steel mills (3). A significant portion of the wastewater generated contains suspended solids and dissolved solids that are inorganic in nature. Most municipal treatment plants are not equipped to handle or treat this type of wastewater.

The only two waste streams generally susceptible to joint treatment are the coke oven wastewaters (ammonia liquor, still bottoms, and light oil recovery wastewaters) and the pickling liquor. The other process wastewaters are high in solids (sub-micron iron oxide dust) and heavy metals. Pretreatment to reduce these waste constituents generally results in an effluent which can be discharged directly to surface waters, for which further joint treatment is not cost effective.

The coke oven process wastewaters are amenable to biological treatment when they constitute only a minor fraction (approximately 25 percent) of the total wastewater flow to the joint treatment facility (2). The cyanide concentration (with its resulting aquatic toxicity characteristics) is the primary consideration in the joint treatment of coke oven process wastes.

The following are characteristics of the process wastewaters:

The still bottoms, containing phenol, constitute the major wastewater source from the coke oven process. Since the beehive oven process utilizes the heat value in the off-gases, only the quench water is discharged as wastewater (1). The gases (CO_2, CO, N, and HCN) leaving the furnace are hot and contain dust particles. The gases also contain water vapor and traces of hydrogen sulfide. In order to clean the exit gas from the blast furnace operations, the gas is generally passed through dust collectors, scrubbers, and coolers. The water used in the scrubbers and coolers is the primary wastewater source in iron manufacture. The waste products from this process are slag and the oxides of iron released as sub-micron dust particles. Precipitators or venturi scrubbers are used to clean the exit gas, and the characteristics of the wastewater discharged from the process will depend primarily on the gas cleaning system. If scrubbers are used, the wastewater generated will be acidic in nature due to the presence of sulfur oxides in the exit gas.

Water is used under high pressure to remove scale and for cooling purposes. The primary wastewaters are the scale-bearing waters and cooling waters containing primarily scale and oil.

Steel pickling to remove oxides and scales is accomplished through solutions of H_2SO_4, HCl, or hydrofluoric acid. The pickled steel is then rinsed with water and coated with oil before proceeding to the next step.

The cold rolling process involves passing unheated metal through rolls for reducing size or thickness, and improving the surface finish.

Plating of steel products is done electrolytically, and is accomplished in either an alkaline or an acid electrolyte solution. If acid electrolyte is used, the process system will consist of alkaline washing, rinsing, pickling, plating, quenching, chemical treating, rinsing, drying, and oiling. The most commonly used metallic coatings are tin, zinc, nickel, chromium, cadmium, copper, aluminum, silver, gold, and lead. Wastewaters generated from cold finishing operations include: rolling solutions, cooling water, plating wastes, pickling rinse waters, and concentrated waste-acid baths. Rolling solutions and cooling water generally contain oil and suspended solids as pollutants. Plating wastes, pickling rinse, and concentrated acid baths may contain various heavy metals (Cr, Cd, Ni, Zn, Sn) as well as cyanides, acids, and alkali.

4. Pretreatment

The pretreatment unit operations which may be necessary for various types of joint treatment processes are shown in Table D-14-2. Even though the wastewaters from the coke oven and cold finishing operations are susceptible to joint treatment, the effluent limitation values for cyanide and heavy metals must be considered in the design of pretreatment facilities.

TABLE D-14-1

Wastewater Characteristics

Blast Furnaces, Steel Works, and Rolling and Finishing Industry

Characteristics	Coke Works	Iron Works	Steel Works	Hot Forming	Cold Finishing
Industrial Operation	Year-round	Year-round	Year-round	Year-round	Year-round
Flow	INTERMITTENT	Continuous	Continuous	Continuous	INTERMITTENT
BOD	Low-Average	Low-Average	Low	Low	Low-Average
TSS	Low	Low-High	Average-High	Low-High	Low-High
TDS	Low	Low	Low	Low	High
COD	Low-Average	Low-Average	Low	Low	Low-Average
Grit	Present	Present	Absent	Absent	Absent
Cyanide	PRESENT	Present	Absent	Absent	PRESENT
Chlorine Demand	High	Low	Low	Low	Low
pH	Neutral	Neutral	Neutral	Neutral	ACIDIC
Color	Absent	Absent	Absent	Absent	Absent
Turbidity	Present	Present	Present	Present	Present
Explosives	Absent	Absent	Absent	Absent	Absent
Dissolved Gases	Present	Present	Present	Absent	Absent
Detergents	Absent	Absent	Absent	Absent	Present
Foaming	Absent	Absent	Absent	Absent	Absent
Heavy Metals	Absent	Present	Present	Present	PRESENT
Colloidal Solids	Present	Absent	Absent	Absent	Present
Volatile Organics	Present	Absent	Absent	Present	Present
Pesticides	Absent	Absent	Absent	Absent	Absent
Phosphorus	DEFICIENT	DEFICIENT	DEFICIENT	DEFICIENT	DEFICIENT
Nitrogen	Adequate	Adequate	DEFICIENT	DEFICIENT	DEFICIENT
Temperature	HIGH	High	High	High	High[1]
Phenol	PRESENT	Present	Absent	Absent	Present
Sulfides	PRESENT	Present	Absent	Absent	Absent
Oil and Grease	Present	Absent	Absent	Present	PRESENT
Coliform (Total)	Absent	Absent	Absent	Absent	Absent

---

[1] Temperature higher than domestic wastewater; may affect design but not harmful to joint treatment.

NOTES: Characteristics which may require pretreatment or are significant to joint treatment plant design are shown in UPPER CASE.

Wastewater characteristics shown do not reflect industrial practices described in Section 2.

TABLE D-14-2

Pretreatment Unit Operations for the Blast Furnaces, Steel Works, and Rolling and Finishing Industry

Pretreatment Sub-Group	Suspended Biological System	Fixed Biological System	Independent Physical-Chemical System
Coke Production	Equalization + Solids Separation	Equalization + Solids Separation	Equalization + Solids Separation
Cold Finishing	Equalization + Oil Separation or Skimming + Chemical Precipitation (heavy metals) + Neutralization	Equalization + Oil Separation or Skimming + Chemical Precipitation (heavy metals) + Neutralization	Equalization + Oil Separation or Skimming + Neutralization

REFERENCES

1. Nemerow, N.L., "Theories and Practices of Industrial Waste Treatment", Addison-Wisley Publishing Co. Inc., Reading, Mass. (1963).

2. "Industry Profile Study on Blast Furnace and Basic Steel Products", Water Quality Office, Contract No. 68-01-0006, Environmental Protection Agency, Washington, D.C. (unpublished).

3. "The Cost of Clean Water, Vol. III, Industrial Waste Profile No. 1, Blast Furnaces and Steel Mills", U.S. Dept. of the Interior, FWPCA (1967).

ORGANIC CHEMICALS INDUSTRY

1. Industry Description

This industry includes Standard Industrial Classifications (SIC) 2811, 2813, 2814, 2815, and 2818.

These classifications include the manufacture of a wide variety of products ranging from industrial gases and fertilizers to dyes, pigments, and petroleum compounds.

The total annual production of organic chemicals in the United States has been estimated to be 120 billion pounds for the year 1969. A major portion of these chemicals falls under Standard Industrial Classifications 2815 and 2818. The important products of the industry are those derived from petroleum fractions.

The Organic Chemicals industry consists of such a complex combination of processes and products that a "typical or average" plant exists only in a statistical sense. The product mix and output of an industry depend primarily on the total economic activity and the demand for products. The Organic Chemicals industry is very dynamic in development of new products and processes.

Considering the number of products involved within the industry (several hundred), this study has been limited to the high-volume products, and only 27 major chemicals are included. These products in combination represent approximately 81 percent of the total organic chemicals manufactured in the United States. A listing of the products covered is shown below in the order of 1970 manufacturing volume (1):

1. Ethylene
2. Benzene
3. Propylene
4. Ethylene Dichloride
5. Toluene
6. Methanol
7. Ethylbenzene
8. Styrene
9. Formaldehyde
10. Vinyl Chloride
11. Ethylene Oxide
12. Xylene (Mixed)
13. Butadiene
14. Ethylene Glycol
15. Ethanol
16. Isopropanol
17. Acetic Acid
18. Cumene
19. Cyclohexane
20. Phenol
21. Acetaldehyde
22. Acetic Anyhdride
23. Terephthalic Acid
24. Dimethyl Terephthalate
25. Acetone
26. Adipic Acid
27. Acrylonitrile

The total annual U.S. production of these 27 organic chemicals amounted to approximately 98 billion pounds for 1970. Depending upon the sequence of production from petroleum sources, chemicals are referred to as either feedstocks or intermediate petrochemicals. Of the 27 chemicals there are 22 intermediate chemicals and five feedstocks (i.e., ethylene, propylene, benzene, toluene, and xylene).

A review of wastewater characteristics indicated that certain products can be grouped together on the basis of pollutants present in the wastewater. Accordingly, the 27 product chemicals covered under this category are divided into three Sub-groups as follows:

Sub-Group 1

1. Benzene
2. Toluene
3. Xylene
4. Cyclohexane
5. Adipic Acid
6. Ethylbenzene
7. Styrene
8. Phenol
9. Terephthalic Acid (TPA)
10. Dimethyl Terephthalate (DMT)
11. Ethylene
12. Ethylene Dichloride
13. Vinyl Chloride (Monomer)
14. Ethanol
15. Acetaldehyde
16. Acetic Acid
17. Acetic Anyhdride
18. Propylene
19. Isopropanol
20. Acetone
21. Cumene
22. Ethylene Oxide
23. Ethylene Glycol

Sub-Group 2

1. Butadiene
2. Methanol
3. Formaldehyde

Sub-Group 3

Acrylonitrile

2. Industrial Practices

The chemical reactions involved in the production of the foregoing chemicals include petroleum reforming, thermal or catalytic cracking, oxidation, alkylation, dehydrogenation, hydration, and chlorination. Most processes use proprietary catalysts to increase product yield and to reduce severe operating conditions and pollution. Water is used extensively both in the process and for cooling purposes.

3. Wastewater Characteristics

The characteristics of process wastewaters from the manufacture of products under each pretreatment group are shown in Table D-15-1.

The characteristics of wastewaters vary from plant to plant, according to the products and processes used. The Organic Chemicals plants generally operate 24 hours a day throughout the year. Depending upon the product mix and the manufacturing process, hourly variations in wastewater volume and loading may occur as a result of certain batch operations (filter washing, crystallization, solvent extraction, etc.). The wastewater collection systems are generally segregated, to permit separate collection of process wastewaters and relatively clean cooling waters. The process wastewaters are usually discharged to a common sewerage system for treatment and disposal.

The process wastewaters from the manufacture of chemicals under Sub-Group 1 generally contain free or emulsified oil, while under Sub-Group 2 generally do not contain oil. Acrylonitrile manufacture (Sub-Group 3) produces a wastewater containing cyanides and substantial quantities of acids.

These wastewaters, in general, contain unreacted raw materials and losses in products, by-products, coproducts, and any auxiliary chemicals used in the process. Detailed analyses for every specific chemical present in the wastewater is difficult and are not generally used to describe the characteristics of wastes. However, the available information indicates that the wastewaters contain: BOD, COD, oil, suspended solids, acidity, alkalinity, heavy metals, and heat.

The wastewaters discharged from the manufacture of products under Sub-Group 1 may contain oil and grease and a series of heavy metals (Fe, Cd, Cu, Co, V, Pd) (2,3). The types and amounts of heavy metals in the wastewater depend primarily on the manufacturing process and the amount and type of catalysts lost from the process. Most catalysts are expensive and, therefore, recovered for reuse. Only unrecoverable catalysts (heavy metals), generally in small concentrations, appear in the wastewater.

The wastewaters generated from the manufacture of products under Sub-Group 2 contain: BOD, acidity or alkalinity (pH

4 to 11), and heavy metals (Cr, Cu, Zn, Hg). These wastewaters are amenable to biological treatment after equalization and neutralization. The production of butadiene may produce a wastewater containing free or emulsified oil; an oil separation device may be required as pretreatment when the oil content in the wastewater exceeds 50 mg/L. Only unrecoverable heavy metals (catalysts), generally in small concentrations, appear in the wastewater.

The manufacture of acrylonitrile produces a highly toxic wastewater which is difficult to treat biologically. The toxicity characteristics have been attributed to the presence of hydrogen cyanide in excessive quantities (500 to 1,800 mg/L). In addition, the wastewater is generally acidic (pH 4 to 6) and contains high concentrations of organic carbon. These wastewaters are generally segregated from other process wastes and disposed of by other means (e.g. incineration). These wastewaters are not generally discharged to municipal collection systems. The pretreatment unit operations developed in the following section do not include the process wastewaters from the manufacture of acrylonitrile (Sub-Group 3).

4. Pretreatment

Table D-15-2 shows the pretreatment unit operations which may be necessary for joint treatment processes.

The heavy metals present in organic chemical wastes are in many cases so low in concentration that heavy metals removal is not required from the standpoint of treatability characteristics. However, the effluent limitations for heavy metals and toxic pollutants may require additional pretreatment (chemical precipitation) for removal of these materials.

The pretreatment unit operations generally consist of equalization, neutralization, and oil separation. In addition, phenol recovery (to reduce the phenol concentration) and spill protection for spent acids and spent caustics may be required in some cases.

Table D-15-1

Wastewater Characteristics

Organic Chemicals

Characteristics	Sub-Group 1	Sub-Group 2	Sub-Group 3
Industrial Operation	Year-round	Year-round	Year-round
Flow	Continuous-Variable	Continuous-Variable	Continuous-Variable
BOD	Average-EXT. HIGH	AVERAGE-HIGH	Low[1]
TSS	Low-High	Low	High
TDS	HIGH	Low-High	High
COD	Average-EXT. HIGH	Average-HIGH	High
Grit	Absent	Absent	Absent
Cyanide	Absent	Absent	PRESENT
Chlorine Demand	High	High	High
pH	ACIDIC-ALKALINE	ACIDIC-ALKALINE	ACIDIC
Color	Low-Average	Low-Average	Low
Turbidity	Low	Low	Low
Explosives	Absent	Absent	Absent
Dissolved Gases	Present	Present	Present
Detergents	Present	Present	Present
Foaming	Present	Present	Present
Heavy Metals	Present	Present	Present
Colloidal Solids	Absent	Absent	Absent
Volatile Organics	Present	Present	Present
Pesticides	Absent	Absent	Absent
Phosphorus	DEFICIENT	DEFICIENT	DEFICIENT
Nitrogen	DEFICIENT	DEFICIENT[2]	Adequate
Temperature	Normal-HIGH[3]	High[3]	No Data
Phenol	Low-High	Present	Absent
Sulfides	Present	Present	Absent
Oil and Grease	Low-HIGH	Low-HIGH	Absent
Coliform (Total)	Low	Low	Low

---

[1] Low BOD is probably due to the toxicity characteristics of this waste.

[2] Adequate when butadiene is manufactured.

[3] Temperature equal to or higher than domestic wastewater; may affect design but not harmful to joint treatment.

NOTES: Characteristics which may require pretreatment or are significant to joint treatment plant design are shown in UPPER CASE.
Wastewater characteristics shown reflect all industrial practices described in Section 2.

Table D-15-2
Pretreatment Unit Operations for the Organic Chemicals Industry

Pretreatment Sub-Group	Suspended Biological System	Fixed Biological System	Independent Physical-Chemical System
1	Oil Separation + Equalization + Neutralization + Spill Protection + Chemical Precipitation[1]	Oil Separation + Equalization + Neutralization + Spill Protection + Chemical Precipitation[1]	Equalization + Neutralization + Chemical Precipitation[1]
2	Oil Separation[2] + Equalization + Neutralization	Oil Separation[2] + Equalization + Neutralization	Equalization + Neutralization

---

[1] Need for chemical precipitation depends on extent of catalyst recovery.

[2] Oil separation required for butadiene manufacture only.

REFERENCES

1. Chemical and Engineering News, (May 17, 1971).

2. "Reference Guidelines for Organic Chemical Industries", Environmental Protection Agency, Washington, D.C. (Unpublished)

3. "Projected Wastewater Treatment Costs in the Organic Chemical Industry", Water Pollution Control Res. Series 12020 GND 07/71, Environmental Protection Agency, Research and Monitoring (July, 1971).

METAL FINISHING INDUSTRY

1. Industry Description

This industry includes Standard Industry Classification (SIC) 3471.

The industries covered under this classification include those primarily engaged in various types of plating, anodizing, coloring, forming, and finishing of metals. The metal-finishing industry operations are related closely to those of many other industries, including transportation (automobile parts and accessories), electrical, and jewelry.

The metal-finishing operation involves cleaning, conversion coating, organic coating, plating, anodizing, coloring, and case hardening. Acid pickling is the most common type of cleaning of metal being prepared for plating. Sulfuric acid is the most commonly used pickling agent, but phosphoric, hydrochloric, hydrofluoric, and other acids are used as well. Alkalies, dichromates, and numerous proprietary compounds are also used in various combinations for descaling, degreasing, desmudging, stripping, brightening, or otherwise preparing different metals (zinc, steel, brass, copper, etc.) for plating or anodizing.

The plating solutions for nickel, chromium copper, cadmium, zinc, tin, and silver may be basically cyanide, acid, or alkaline. Anodizing is done either in sulfuric acid or in chromate solutions. Colorizing is accomplished with dyes, nickel acetate, and chromates. Cyanides are used in case hardening.

2. Wastewater Characteristics

The characteristics of the process wastewaters from the industry are shown in Table D-16-1.

The metal-finishing industry usually generates a continuous stream of rinse waters containing dilute concentrations of heavy metals and cyanides and intermittent batch dumpings of spend acid and cleaning solutions. The nature of metal-finishing operations and the consequent fluctuating (cyclic) characteristics of the wastewater should be taken into consideration in the design of treatment facilities.

Water is used extensively in metal-finishing processes to clean, strip, pickle, and rinse the metal products before and after plating operations. The rinse waters constitute the major volume of wastewaters, while spent solutions discharged intermittently add major pollutants to the total effluent. The wastewaters contain, in general, spent acids, alkalis, oil and grease, detergents, cyanides, and various heavy metals (Cr, Ni, Cu, Ag, Fe, Zn, and Sn). The metal-finishing plants differ from one another with respect to their processes, metals, and chemicals, and the characteristics of wastewater may vary widely from one to another. However, their wastewaters all contain primarily inorganic pollutants, particularly heavy metals. In addition, the wastewaters frequently are highly toxic due to the presence of cyanides and heavy metals (1,2,3).

In general, the types of wastewaters from metal-finishing industries are:

1. Acid wastes
2. Alkaline wastes
3. Heavy metals wastes
4. Cyanide-bearing wastes
5. Miscellaneous wastes (dyes, soluble and floating oils, etc.)

Any of these wastewaters may occur as either dilute rinse waters or concentrated baths. Except for the cyanide-bearing wastes, the wastewaters are generally connected to a common sewerage system for treatment and disposal. The cyanide wastes usually are collected in a segregated sewer system in order to prevent the release of toxic hydrogen cyanide gas under acidic conditions. However, the cyanide wastes can be mixed with other waste streams provided that any acid streams are neutralized prior to mixing with the cyanide waste stream (4,5,6).

The major constituents in the wastewaters generated from metal-finishing operations are cyanides, metal ions, (Cr^{6+}, Ni, Fe, Cu, Ag, and Sn), oil and grease, organic solvents, acids, and alkalis. The wastewaters characteristically are so toxic and corrosive to sewers and equipment that they require pretreatment before discharge to municipal sewers.

A wide variety of processes are used in metal finishing operations, resulting in widely varying wastewater characteristics. Typically, these wastewaters have poor treatability characteristics without adequate pretreatment.

3. Pretreatment

The pretreatment unit operations for various types of joint treatment facilities are shown in Table D-16-2.

The pretreatment processes generally involve separate treatment of cyanide wastes and other acid wastes containing metal ions. The cyanide wastes can be treated with ferrous sulfate and lime to convert highly toxic cyanides to less toxic cyanates or cyanide complexes, or can be oxidized to CO_2 and N_2 with chlorine under alkaline conditions. The acid waste streams are treated first to reduce hexavalent chromium to trivalent chromium, using ferrous sulfate, scrap iron, or sulfur dioxide, and then precipitating the metal ions (Cr^{3+}) as metal hydroxides.

In addition to the effluent limitations and the processes shown in Table D-16-2, the degree of reduction in heavy metals waste loadings should consider the sludge handling and disposal methods used for the combined domestic and metal finishing wastewaters. Some processes (e.g. anaerobic digestion) concentrate these metals, and this can lead to process failure unless adequate pretreatment is provided.

Table D-16-1

Wastewater Characteristics

Metal Finishing Industry

Characteristics	
Industrial Operation	Year-round (BATCH)
Flow	Continuous-VARIABLE
BOD	Low
TSS	Average-High
TDS	HIGH
COD	Low
Grit	Present
Cyanide	HIGH
Chlorine Demand	HIGH
pH	ACIDIC
Color	Present
Turbidity	Present
Explosives	Absent
Dissolved Gases	Present
Detergents	Present
Foaming	Absent
Heavy Metals	HIGH
Colloidal Solids	Absent
Volatile Organics	Present
Pesticides	Absent
Phosphorus	Present
Nitrogen	Present
Temperature	Normal[1]
Phenol	Low
Sulfides	Absent
Oil and Grease	Present
Coliform (Total)	Absent

[1] Temperature similar to domestic wastewater

NOTE: Characteristics which may require pretreatment or are significant to joint treatment plant design are shown in UPPER CASE.

TABLE D-16-2

Pretreatment Unit Operations for the Metal Finishing Industry

Suspended Biological System	Fixed Biological System	Independent Physical Chemical System
Equalization + Neutralization + Cyanide Removal + Chromium Reduction + Chemical Precipitation (Heavy Metals)+ Solids Separation	Equalization + Neutralization + Cyanide Removal + Chromium Reduction + Chemical Precipitation (Heavy Metals) + Solids Separation	Equalization + Cyanide Removal + Chemical Precipitation + Neutralization

---

[1] Chemical precipitation may not be needed, depending on the processes used in the independent physical chemical joint treatment plant.

REFERENCES

1. Barnes, E.G., and Weinberger, L.W., "Complex Metal Finishing Wastes Licked by Effective Chemical Treatment", Wastes Engineering, 124-127 (1957).

2. Barnes, G.E., "Treatment Works for Plating Wastes Containing Toxic Metals and Cyanides", Water and Sewage Works, 94, 8, (1947).

3. Nemerow, N.L., "Theories and Practices of Industrial Waste Treatment", Addison-Wesley Publishing Co., Inc., Reading, Mass. (1963).

4. "An Investigation of Techniques for Removal of Cyanide from Electroplating Wastes", Water Pollution Control Research Series, 12010-EIE 11/71, EPA, Washington, D.C. (1971).

5. "An Investigation of Techniques for Removal of Chromium from Electroplating Wastes", Water Pollution Control Research Series, 12010-EIE 3/71, EPA, Washington, D.C. (1971).

6. "Ultrathin Membranes for Treating Metal Finishing Effluents for Reverse Osmosis", Water Pollution Control Research Series, 12010-DRH 11/71, EPA - Research and Monitoring (1971).

Annex 17

Other Industries

Six industries have been included in this group, on the basis of the following considerations:

1. Wastewaters from the industry contain only inorganic waste constituents.
2. Wastewaters from the industry are not usually discharged to joint treatment plants.

The following industries are included in this group:

1. Inorganic Fertilizer
   (SIC 2071)
2. Electric and Steam Generation
   (SIC 4911, 4961)
3. Aluminum
   (SIC 3334, 3341, 3361)
4. Flat Glass, Cement, Lime, Concrete Products, Gypsum, and Asbestos
   (SIC 3211, 3241, 3274, 3275, 3292)
5. Inorganic Chemicals
   (SIC 2812, 2819)
6. Industrial Gas Products
   (SIC 2813)

Two tables are provided for each of these six industries; the first shows the wastewater characteristics, and the other shows pretreatment unit operations for various joint treatment processes.

Table D-17-1

Wastewater Characteristics

Inorganic Fertilizer

Characteristics	Phosphoric Acid Normal Super Phosphate Triple Super Phosphate Mono-Ammonium Phosphate Di-Ammonium Phosphate N-P-K Fertilizers	Ammonia	Ammonium Nitrate Urea Ammonium Sulfate
Industrial Operation	Year-Round	Year-Round	Year-Round
Flow	Continuous	Continuous	Continuous
BOD	Low-Average	Low	Low-Average
TSS	Average-High	Low-Average	Low-Average
TDS	HIGH	HIGH	HIGH
COD	Low-Average	Low	Low-Average
Grit	Absent	Absent	Absent
Cyanide	Absent	Absent	Absent
Chlorine Demand	Low	Low	Low
pH	ACID	ALKALINE	ALKALINE
Color	No Data	No Data	No Data
Turbidity	No Data	No Data	No Data
Explosive Chemicals	Absent	Absent	Absent
Dissolved Gases	PRESENT	Absent	Absent
Detergents	Absent	Absent	Absent
Foaming	No Data	No Data	No Data
Heavy Metals	Absent	Absent	Absent
Colloidal Solids	Absent	Absent	Absent
Volatile Organics	Absent	Absent	Absent
Pesticides	Absent	Absent	Absent
Phosphorus	Adequate	DEFICIENT	Adequate
Nitrogen	Adequate	Adequate	Adequate
Temperature	Normal-High[1]	Normal-High[1]	Normal-High[1]
Phenol	No Data	No Data	No Data
Sulfide	No Data	No Data	No Data
Oil & Grease	Absent	PRESENT[2]	Absent
Coliform (Total)	Absent	Absent	Absent

---

[1] Temperature equal to higher than domestic wastewater; affect design but not harmful to joint treatment.

[2] Oil present in the wastewater is mineral in origin.

NOTE: Characteristics which may require pretreatment or are significant to joint treatment plant design are shown in UPPER CASE.

Table D-17-2

Pretreatment Unit Operations for the Inorganic Fertilizers Industry

Pretreatment Group	Suspended Biological System	Fixed Biological System	Independent Physical-Chemical System
Phosphoric Acid Normal Super Phosphate Triple Super Phosphate Mono-Ammonium Phosphate Di-Ammonium Phosphate N-P-K Fertilizers	solids separation + neutralization	solids separation + neutralization	solids separation + neutralization
Ammonia	neutralization + oil separation	neutralization + oil separation	neutralization + oil separation
Ammonium Nitrate Urea Ammonium Sulfate	neutralization	neutralization	neutralization

Table D-18-1

Wastewater Characteristics

Electric and Steam Generation

Characteristic	
Industry Operation	Year-Round
Flow	INTERMITTENT
BOD	Low
TSS	Low
TDS	High
COD	Low
Grit	Low
Cyanide	Present[1]
Chlorine Demand	Low
pH	ACIDIC-ALKALINE
Color	Low
Turbidity	Low
Explosive Chemicals	Absent
Dissolved Gases	Absent
Detergents	Present
Foaming	Present
Heavy Metals	PRESENT
Colloidal Solids	Absent
Volatile Organics	Present
Pesticides	Absent
Phosphorus	DEFICIENT
Nitrogen	DEFICIENT
Temperature	HIGH[2]
Phenol	Present[3]
Sulfide	Absent
Oil and Grease	Present
Coliform (Total)	Absent

---

[1] Cyanide may be present if cooling water is also discharged to the sewers.

[2] Temperature higher than domestic wastewater; may require cooling as pretreatment.

[3] Phenol may be used in cooling water treatment.

NOTE: Characteristics which may require pretreatment or are significant to joint treatment plant design are shown in UPPER CASE.

Table D-18-2

Pretreatment Unit Operations for the Electric and Steam Generation Industry

Suspended Biological System	Fixed Biological System	Independent Physical-Chemical System
Equalization (cooling) + Neutralization + Chemical Precipitation (heavy metals) + Cyanide Oxidation	Equalization (cooling) + Neutralization + Chemical Precipitation (heavy metals) + Cyanide Oxidation	Equallation (cooling) + Neutralization + Chemical Precipitation (heavy metals) + Cyanide Oxidation

Table D-19-1

Wastewater Characteristics

onferrous Metals - Aluminum

Characteristics	Bauxite Refining Primary Smelting	Direct Chill Ingot Coating and Foundry Rolling, Drawing and Extruding
Industry Operation	Year-round	'ear-round
Flow	Continuous	Continuous
BOD	Low	Low
TSS	HIGH	HIGH
TDS	Low	Low-Average
COD	Low	Low
Grit	PRESENT[1]	Absent
Cyanide	Present	Absent
Chlorine Demand	Low	Low
pH	'eutral	EUTRAL-ACID
Color	High	Average
Turbidity	High	Average
Explosive Chemicals	Absent	Absent
Dissolved Gases	PRESENT[2]	PRESENT[2]
Detergents	Absent	Absent
Heavy 'etals	Present	Absent
Colloidal Solids	Absent	Absent
Volatile Organics	Absent	Absent
Pesticides	Absent	Absent
Phosphorus	DEFICIENT	Deficient-Adequate[4]
Nitrogen	DEFICIENT	DEFICIENT
Temperature	Normal-HIGH	Normal-HIGH
Phenol	Absent	Absent
Sulfide	Absent	Absent
Oil and Grease	Present	Present[5]
Coliform (Total)	Absent	Absent

---

[1] Present in bauxite refining wastewater.

[2] Fluorine is generally present in scrubber water.

[3] Chlorine is present in casting, foundry, and secondary smelting scrubber waters.

[4] Phosphate in high concentration (1,000 mg/L) is present only when can stock is coated in preparation for painting by the can manufacturer.

[5] Oil and Grease may be present in emulsified form; not animal or vegetable origin.

NOTE: Characteristics which may require pretreatment or are significant to joint treatment plant design are shown in UPPER CASE.

Table D-19-2

Pretreatment Unit Operations for the Aluminum Industry

Pretreatment Group	Suspended Biological System	Fixed Biological System	Independent Physical-Chemical System
Bauxite Refining Primary Smelting	solids separation	solids separation	solids separation
Direct Chill Ingot Casting and Foundry Rolling, Drawing, Foundry Extruding Secondary Smelting	oil separation + neutralization + chemical precipitation (phosphate removal)	oil separation + neutralization + chemical precipitation (phosphate removal)	oil separation + neutralization + chemical precipitation (phosphate removal)

Table D-20-1

Wastewater Characteristics

Glass, Cement, Lime, Concrete Products, Asbestos and Gypsum Products

Characteristic	Flat Glass	Mirrors	Cement & Lime	Concrete Products	Asbestos & Gypsum
Industry Operation	Year-round	Year-round	Year-round	Year-round	Year-round
Flow	Continuous	Continuous	Continuous	Continuous	Continuous
BOD	Low	Low	Low	Low	Low
TSS	Low-HIGH	HIGH	HIGH	Low-HIGH	Low-HIGH
TDS	Low-HIGH	HIGH	HIGH	LOW-HIGH	No data
COD	Low	Low	Low	Low	Low
Grit	PRESENT	PRESENT	Absent	PRESENT	Absent
Cyanide	Absent	Absent	Absent	Absent	Absent
Chlorine Demand	No Data	No Data	No Data	No Data	No Data
pH	Neutral	ALKALINE	ALKALINE	ALKALINE	Neutral
Color	Absent	Absent	Absent	Absent	Absent
Turbidity	Present	Present	Present	Present	Present
Explosive Chemicals	Absent	Absent	Absent	Absent	Absent
Dissolved Gases	Absent	Absent	Absent	Absent	Absent
Detergents	PRESENT	PRESENT	PRESENT	PRESENT	PRESENT
Foaming	Absent	Absent	Absent	Absent	Absent
Heavy Metals	Absent	Present	Absent	Absent	Absent
Colloidal Solids	PRESENT	PRESENT	PRESENT	PRESENT	PRESENT
Volatile Organics	Absent	Absent	Absent	Absent	Absent
Pesticides	Absent	Absent	Absent	Absent	Absent
Phosphorus	PRESENT	PRESENT	DEFICIENT	DEFICIENT	DEFICIENT
Nitrogen	DEFICIENT	DEFICIENT	DEFICIENT	DEFICIENT	DEFICIENT
Temperature	Normal[2]	Normal[2]	Normal-High[2]	Normal[2]	Normal-High[2]
Phenol	Absent	Absent	Absent	Absent	Absent
Sulfide	Absent	Absent	Absent	Absent	Absent
Oil and Grease	ABSENT[1]	Absent	Absent	Absent	Absent
Coliform (Total)	Absent	Absent	Absent	Absent	Absent

---

[1] Present in automotive glass and glass bottles manufacturing wastewaters.

[2] Temperature equal to or greater than domestic wastewater; may affect design but not harmful to joint treatment.

NOTE: Characteristics which may require pretreatment or are significant to joint treatment plant design are shown in UPPER CASE.

Table D-20-2

Pretreatment Unit Operations for the
Glass, Cement, Lime, Concrete Products, Asbestos, and Gypsum Products Industry

Pretreatment Group	Suspended Biological System	Fixed Biological System	Independent Physical Chemical System
Flat Glass	grit removal + solids separation	grit removal + solids separation	grit removal + solids separation
Mirrors	grit removal + neutralization + chemical precipitation (heavy metals)	grit removal + neutralization + chemical precipitation (heavy metals)	grit removal + neutralization + chemical precipitation (heavy metals)
Cement & Lime	neutralization	neutralization	neutralization
Concrete Products	grit removal + neutralization	grit removal + neutralization	grit removal + neutralization
Asbestos & Gypsum Products	solids separation	solids separation	solids separation

Table D-21-1

Wastewater Characteristics

Inorganic Chemicals

Characteristic	Calcium Carbide Sodium Chloride Sodium Tripolyphosphate	Chlorine, Etc.	Hydrogen Peroxide Sodium Dichromate Sodium Sulfate	Aluminum Chloride, Etc.
Industry Operation	Year-Round	Year-Round	Year-Round	Year-Round
Flow	Continuous	Continuous	Continuous	Continuous
BOD	Low	Low	Low	Low
TSS	No Data	No Data	No Data	No Data
TDS	AVERAGE[1]	HIGH	HIGH	HIGH
COD	Low	Low	Low	Low
Grit	Absent	Absent	Absent	Absent
Cyanide	Absent	Absent	PRESENT[2]	Absent
Chlorine Demand	Low	Low	Low	Low
pH	Neutral	ACID-BASIC	ACID-BASIC	ACID-BASIC
Color	No Data	No Data	No Data	No Data
Turbidity	No Data	No Data	No Data	No Data
Explosive Chemicals	Absent	Absent	Absent	Absent
Dissolved Gases	Absent	Absent	Absent	Absent
Detergents	Absent	Absent	Absent	Absent
Foaming	No Data	No Data	No Data	No Data
Heavy Metals	Absent	PRESENT[3]	PRESENT	Absent
Colloidal Solids				
Volatile Organics	Absent	Absent	Absent	Absent
Pesticides	Absent	Absent	Absent	Absent
Phosphorus	DEFICIENT[4]	DEFICIENT	DEFICIENT	DEFICIENT
Nitrogen	DEFICIENT	DEFICIENT	DEFICIENT	DEFICIENT
Temperature	Normal-high	Normal-high	Normal-high	Normal-high
Phenol	No Data	No Data	No Data	No Data
Sulfide	No Data	No Data	No Data	No Data
Oil and Grease	Absent	Absent	Absent	Absent
Coliform (Total)	No Data	No Data	No Data	No Data

---

[1] NaCl wastes have high salt concentrations.

[2] Cyanide generated by electrolytic process for hydrogen peroxide.

[3] Downs cell process for chlorine doesn't generate heavy metals.

[4] Sodium Triphosphate Wastewater will have very high phosphate concentration (≈2000 mg/l)

NOTE: Characteristics which may require pretreatment or are significant to joint treatment plant design are shown in UPPER CASE.

Table D-21-2

Pretreatment Unit Operations for the Inorganic Chemicals Industry

Pretreatment Group	Suspended Biological System	Fixed Biological System	Independent Physical-Chemical System
Calcium Carbide Sodium Chloride Sodium Tripolyphosphate	pretreatment not required	pretreatment not required	pretreatment not required
Chlorine Sodium Hydroxide Potassium Hydroxide Sodium Metal Hydrochloric Acid	neutralization + chemical precipitation (heavy metals) + equalization	neutralization + chemical precipitation (heavy metals) + equalization	neutralization + chemical precipitation (heavy metals)
Hydrogen Peroxide Sodium Dichromate Sodium Sulfate	neutalization + chemical precipitation (heavy metals)	neutralization + chemical precipitation (heavy metals)	neutralization + chemical precipitation (heavy metals)
Aluminum Chloride Aluminum Sulfate Hydrofluoric Acid Nitric Acid Sodium Bicarbonate Sodium Silicate Sodium Sulfite Sulfuric Acid Sodium Carbonate	neutralization	neutralization	neutralization

Table D-22-1

Wastewater Characteristics

Industrial Gases

Characteristic	Hydrogen, Nitrogen, Oxygen, and Carbon Dioxide
Industry Operation	Year-Round
Flow	Continuous
BCD	Low
TSS	Low-average
TDS	Low-average
COD	Low
Grit	Absent
Cyanide	Absent
Chlorine Demand	Low
pH	ACID-BASIC
Color	Low
Turbidity	Low
Explosive Chemicals	Absent
Dissolved Gases	Absent
Detergents	Absent
Foaming	No Data
Heavy Metals	Absent
Colloidal Solids	Absent
Volatile Organics	Absent
Pesticides	Absent
Phosphorus	DEFICIENT
Nitrogen	DEFICIENT
Temperature	Average-high
Phenol	Absent
Sulfide	Absent
Oil and Grease	PRESENT
Coliform (Total)	Absent

---

[1] Wastewaters are constant over the daily operating period.

NOTE: Characteristics which may require pretreatment or are significant to joint treatment plant design are shown in UPPER CASE.

Table D-22-2

Pretreatment Unit Operations for the Industrial Gases Industry

Industry	Suspended Biological System	Fixed Biological System	Independant Physical-Chemical System
Hydrogen Nitrogen Carbon Dioxide Oxygen	oil separation + neutralization	oil separation + neutralization	oil separation + neutralization

[1] Oil Separation required to reduce mineral oil concentration below 50 mg/L.

U.S. GOVERNMENT PRINTING OFFICE: [illegible]